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STUDIES IN DIBENZOYLETHYLENES

- by -

Nandoo Mal Khanna, M.Sc. (Delhi).

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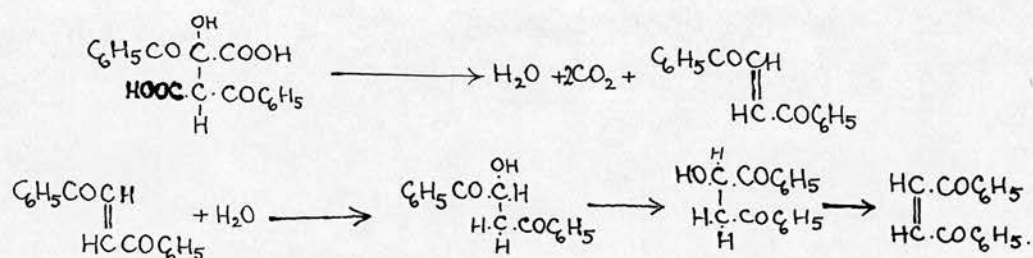
GENERAL INTRODUCTION

The unsaturated 1,4-diketones of the general type $\text{ArCOCH}=\text{CHCOAr}$ are well known and research in this field of Organic Chemistry has attracted the attention of numerous workers. Still amid the complexities of Organic Chemistry it is but natural that certain aspects of the subject should attract widespread notice while other equally important problems should be left unnoticed.

The unsaturated γ -diketones are no exception to this. A glance at the literature reveals a good deal of information about the methods of preparation of dibenzoyl ethylenes and their alkyl, alkoxy and halogen substituted derivatives and through these the preparation of diaryl ethanes which readily pass into furanes and pyrroles, yet there is little reference about the preparation of those compounds in which auxochromic groups such as hydroxyl or amino are present. Likewise one comes across a mass of literature concerning the mechanism of their reduction by various means, yet one finds that nothing has so far been published about the reduction of unsaturated 1,4-diketones by such specific reagents as aluminium-isopropoxide. Several other instances can be quoted where some important problems still await solution.

Studies in dibenzoylethylenes and their various substituted derivatives have been and are being extensively prosecuted - different methods being known for their synthesis.

Paal and Schulze (Ber.1900,33,3800) who were the first in this field, obtained a mixture of the stereoisomeric dibenzoylethylenes by heating dibenzoyl malic acid.



whereas Smedley (J.C.S.1909,95,219) claimed to have prepared the yellow variety by condensing benzoyl-formaldehyde and acetophenone in the presence of an excess of acetic anhydride.

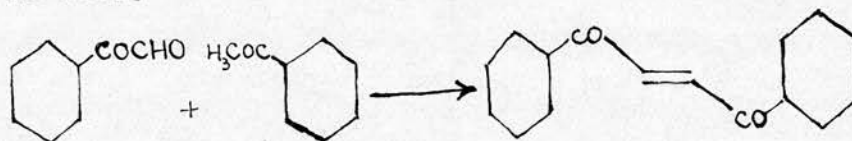
This work was repeated by Weygand and Lanzendorf (J.pr.Chem.1938,151,204), and these workers found that with the acetic anhydride a colourless substance (m.p.112°C) corresponding to

$\text{C}_6\text{H}_5\text{COCH}(\text{OOCCH}_3)\text{CH}_2\text{CO} \text{C}_6\text{H}_5$ (I) was obtained which at 200° gave dibenzoylethylene (yellow isomer).

According to these workers, when glacial acetic acid was used instead of acetic anhydride, 1,2-dibenzoyl-ethanol-1 ($\text{C}_6\text{H}_5\text{COCH(OH)CH}_2\text{CO} \text{C}_6\text{H}_5$) was obtained which on heating with acetic anhydride yielded a product identical with I above.

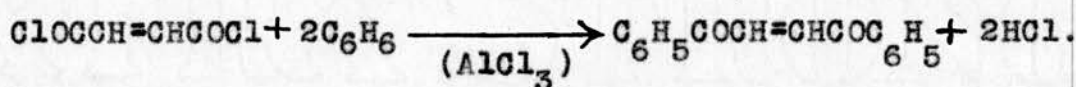
Weygand /

Weygand and Lanzendorf (loc.cit.) found that condensation however, does take place when glacial acetic acid with a trace of concentrated sulphuric acid is used. Compounds such as p-(mono)alkyl-dibenzoylethylenes are conveniently obtained by this method:



These methods have their own disadvantages in that the yields are poor and some expensive and laborious stages are involved.

A much better synthesis was next developed by J.B. Conant and R.E. Lutz (J.A.C.S., 1923, 45, 1303) who were able to obtain the yellow isomer of dibenzoylethylene in good yields (60-75%) by the action of fumaryl chloride on benzene in the presence of aluminium chloride.

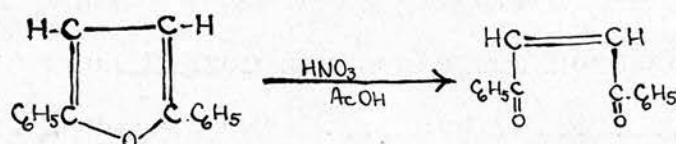


Replacing benzene with toluene, chloro or bromobenzenes etc., in a similar Friedel Crafts reaction, the same authors obtained the corresponding derivatives of dibenzoylethylene.

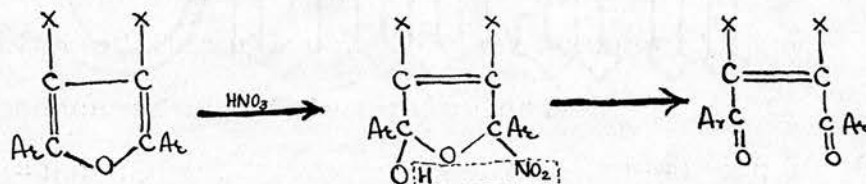
Oddy (J.A.C.S., 1923, 45, 2156) during the preparation of ditoluylyl-ethylene by a Friedel Crafts reaction as above, reported to have obtained a substance which melted at 134.5°C. Weygand and Lanzendorf (loc.cit.) were unable to repeat Oddy's work /

Oddy's work but suggested that Oddy's product might be a metastable modification with the transition temperature at about 144°C .

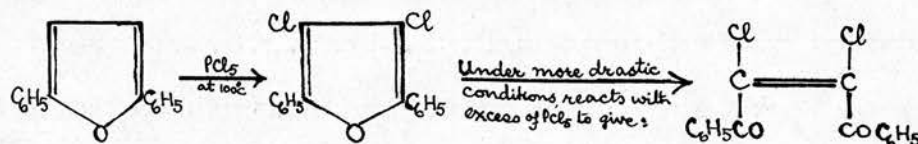
The preparation of dibenzoyl ethylenes was carried a stage further by Lutz and Wilder (J.A.C.S., 1934, 56, 978) when they obtained (in excellent yield - 80%) the various cis-unsaturated 1,4-diketones by the nitric-glacial acetic acid oxidation of the corresponding 2,5 diphenylfurans, (Cf. also Zinin, J.pr.Chem.(I), 101, 164, (1867)):



According to these investigators, the reaction mechanism may be represented as:



Closely related to it, is the reaction between PCl_5 and diphenyl dichlorofuran, resulting eventually in the formation of cis-dibenzoyl dichloroethylene (Lutz and Wilder, J.A.C.S., 1934, 56, 2145), this reaction being assumed to proceed as follows:-

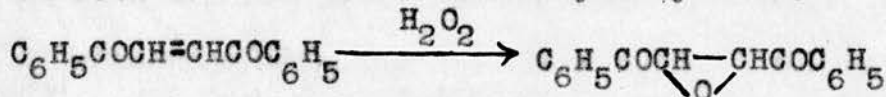


An entirely different method was suggested by Bogoslovskii (J.Gen.Chem.U.S.S.R., 14, 993-4 (1944): C.A. 39, 4600 (1945)) when he reported that sym-dibenzoyl ethylene /

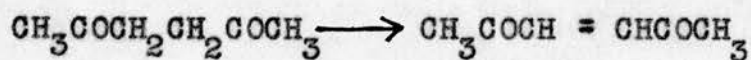
sym-dibenzoyl ethylene may be obtained (in 58-71% yields) by treating a warm alcoholic solution of phenacylchloride with aqueous KOH.

Following this, Fuson and Johnson (J.A.C.S., 1946, 68, 1668-9) however, were unable to prepare sym-dimesityl-ethylene by treating α -chloroacetomesitylene in dioxan with 10% aq. sodium hydroxide solution, alcoholic potassium hydroxide solution or sodium ethoxide.

But the same authors, (Fuson and Johnson, loc. cit.) found that reacting α -chloroacetomesitylene with sodium hypochlorite or hypiodite yielded a halogen free compound ^{and} which proved to be the coupling product sym-dimesityl ethylene ($C_9H_{11}COCH=CHCOC_9H_{11}$); although coupling acetophenone in the same way resulted in the formation of the oxide of expected olefin, sym-dibenzoyl-ethylene: ($C_6H_5COCH \begin{smallmatrix} \diagup O \diagdown \end{smallmatrix} CHCOC_6H_5$). This compound had already been prepared (Lutz and Wilder J.A.C.S., 1934, 56, 1987), by the action of hydrogen peroxide on both cis and trans dibenzoyl ethylenes:



In the aliphatic series, on the other hand, diacetylene was prepared by the selenious acid oxidation of acetyl acetone by Armstrong and Robinson, (J.C.S., 1934, 1650).



The reaction is assumed to take a course analogous to /

to that of ethyl succinate which Astin Riley and Newman (J.C.S.1933,391) found to be oxidized by selenious acid with the formation of ethyl fumarate and ethyl hydrogen fumarate.

Diacetylene thus obtained was pale yellow and was assumed to possess the trans/configuration by analogy with the dibenzoyl-ethylenes of which the cis form is colourless and the trans is yellow. (Conant and Lutz - loc.cit.)

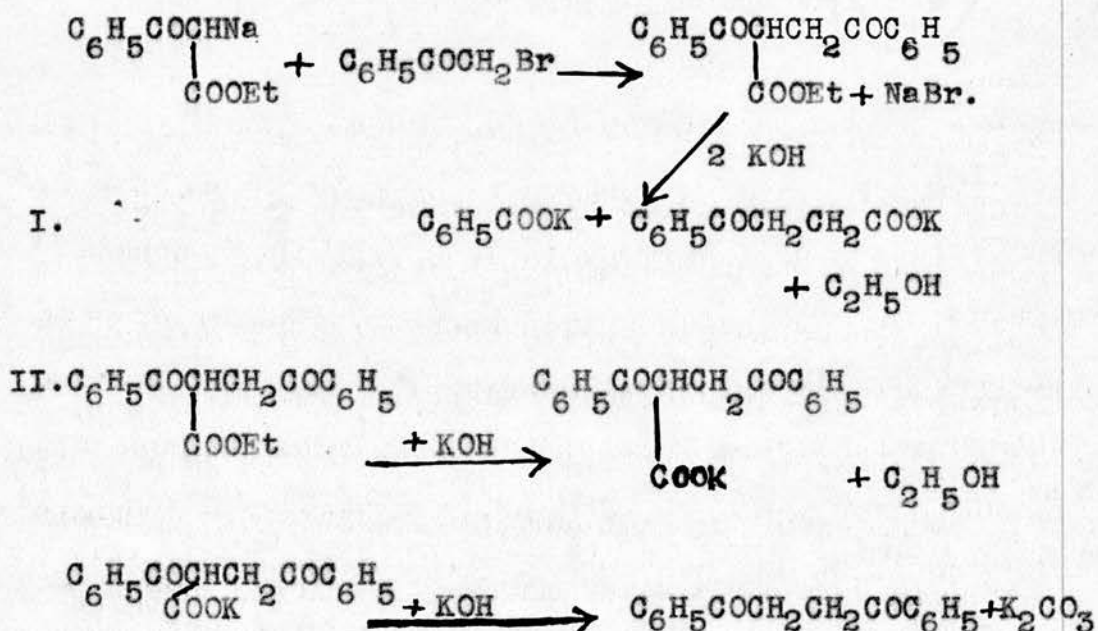
Armstrong and Robinson (loc.cit.) also reported, in the same experiment to have obtained an uncrystallizable material which they assumed to be a mixture of the isomeric diacetylenes. They might have obtained a greater yield of the trans-isomer by/a catalyst, since it is well known that in the dibenzoylenes the colourless or cis-modification rearranges back under the influence of the above catalysts.

Prior to the work described in the present thesis, there appeared to be no published work on the oxidation of diphenacyl and its various substituted derivatives by selenious acid etc., to dibenzoylene and the corresponding substituted derivatives, although 4-4'-dimethyldiphenacyl is oxidized by HNO_3 to yield p-toluic acid (Claus, Ber.20,1377,(1887)), while CrO_3 in acetic acid gives a mixture of $\text{CH}_3\text{C}_6\text{H}_4\text{COCH}_2\text{CH}_2\text{COC}_6\text{H}_4\text{COOH}$ and /

and $\text{HOOC}\text{C}_6\text{H}_4\text{COCH}_2\text{CH}_2\text{COC}_6\text{H}_4\text{COOH}$ -(Limpricht and Doll, Annalen, 312, 115).

Diphenacyl itself has been prepared in a variety of ways: Claus. (Ber., 1887, 20, 1375) obtained it by the Friedel Crafts reaction using succinyl chloride, benzene and aluminium chloride. The yields however, have been reported to be low owing to the fact that a greater part of the acid chloride reacts in unsymmetrical form.

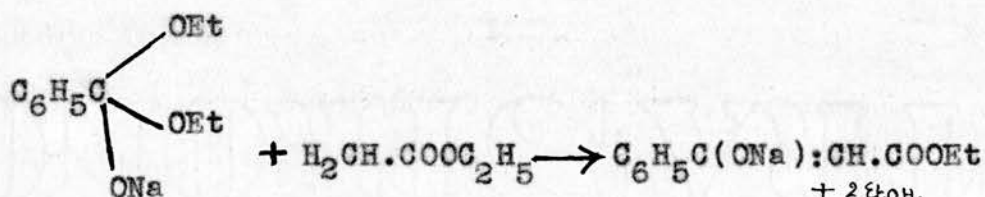
Kapf and Paal (Ber., 21, 3056) obtained diphenacyl (in 20-25% yield) from Phenacylbenzoyl acetic ester and KOH by allowing the mixture to stand for eight to ten days at ordinary temperature. The same authors had earlier found (Ber. 21, 1485) that warming with KOH yields benzoic acid and benzoyl-propionic acid.



A few years later Knorr and Scheidt (Ber. 1894, 27, 1168) described the preparation of diphenacyl from ethyl dibenzoyl succinate by warming with 3% aq. NaOH solution /

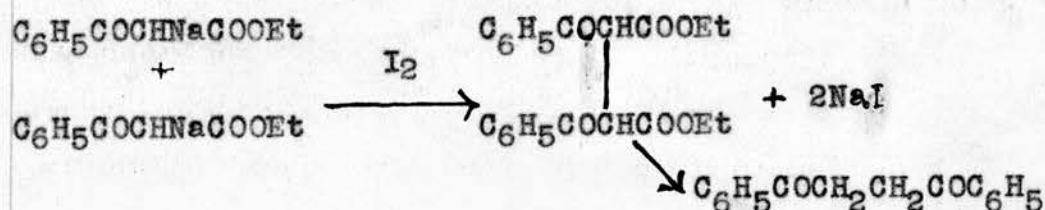
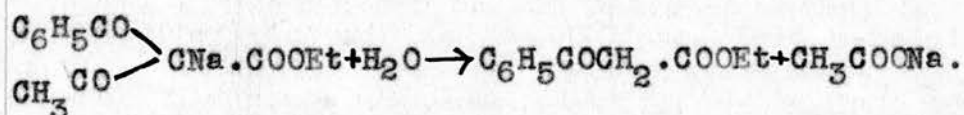
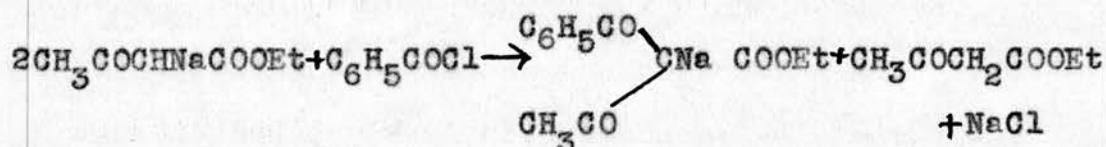
solution on a water bath or by heating with water at 150/170°C or with alcohol at 250°C.

Ethyl dibenzoylsuccinate itself was obtained by Perkin (J.C.S., 1885, 47, 263) from iodine and ethyl benzoylsodioacetate; the latter (i.e. the sodium compound) in its turn being prepared, first by Claisen, by reacting a mixture of ethyl benzoate and ethyl acetate with sodium (Ber., 1887, 20, 653)



although a few years later (1896), the same author (Claisen, Annalen, 291, 67) described a more elaborate method for preparing ethyl benzoylacetate which consisted in acting on two molecules of ethyl sodio acetoacetate with benzoylchloride and subsequently decomposing the sodium compound of ethyl benzoyl aceto acetate thus produced by boiling with ammonia and NH_4Cl .

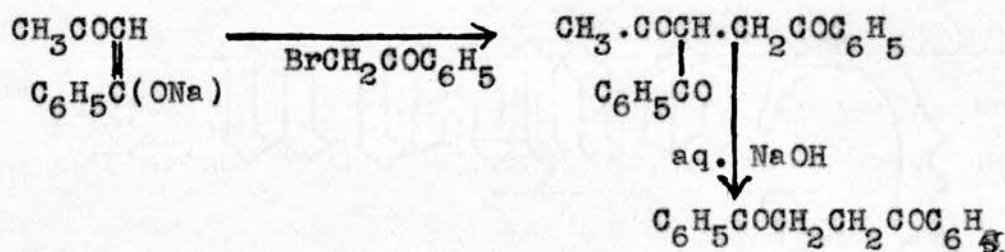
The whole series of reactions is represented as follows:



These two methods have certain disadvantages for not only are costly reagents required, but the yields are low and the different stages laborious.

Perkin and co-workers (J.C.S.1886,49,453;1904,85,148) also prepared ethyl diortho and diparanitrobenzoyl succinates by an identical series of reactions. No yields were quoted by these workers, nor have the products of hydrolysis with alkalies been described.

Bodforss (Ber.1918,51,198-199) in an experiment to condense benzoylacetone with phenacylbromide obtained a compound ($C_{18}H_{16}O_3$) which he named as acetyldiphenacyl. This, on being warmed with aq. *sub* alkalies, gave diphenacyl.



*Na-EXTRA - 2 days
room temp.
no yield quoted.*

Fritz (Ber.28,3033) obtained diphenacyl by reducing α -and β -bromdiphenacyl with zinc dust in alcohol.

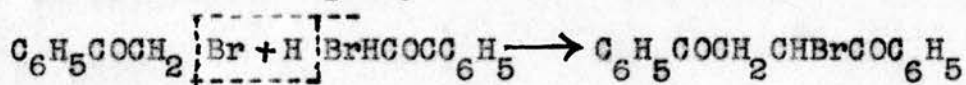
Fritz.(Ber.29,1751) next substituted magnesium powder for zinc dust, and obtained diphenacyl in excellent yields by heating one part of β -bromdiphenacyl (α -bromdiphenacyl being converted by boiling alcohol into the β -variety), fifty parts of alcohol and two to three parts of magnesium powder. The reaction is assumed to be a very simple one in which the chief loss is in the transformation of $C_6H_5COCH_2Br$ into β -bromdiphenacyl

Paal and Stern (Ber.32,531) followed Fritz and they successfully reduced α - and β -chlorodiphenacyl in alcoholic solution with zinc dust and obtained diphenacyl.

Working along the same lines, Paal and Schulze (Ber.36,3413) obtained diphenacyl by reducing β -iododiphenacyl in alcoholic solution with magnesium powder.

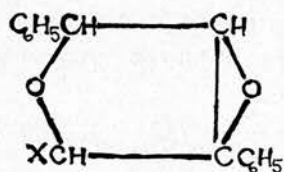
Ajello (Gazz.Chim.Ital.,1937,67,608;C.A.1938,32 4566) suggested the use of aq.KOH instead of NaOEt as the condensing agent. According to this worker $C_6H_5COCH_2Br$ is then readily converted into $C_6H_5COCHBrCH_2COC_6H_5$, and the m.p. quoted is $136^\circ C$. Ajello's work appeared to us to be faulty and it was necessary therefore to repeat his work.

Widman (Ber.,1909,42,3261;Annalen,1913,400,86) although able to obtain diphenacyl by the reduction of bromdiphenacyl with magnesium powder in alcohol, did not agree with Fritz (Ber.,28,3033) and Paal and Schulze (Ber.,35,168,36,2411) who had said that bromdiphenacyl might be represented as being formed in the following way:



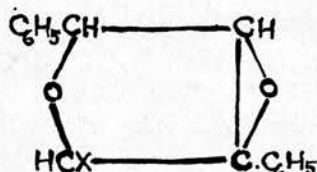
Widman (loc.cit.) was of the opinion that α - and β -halogendiphenacyl possess the following structures /

structures:



Cis—

[α -“halogendiphenacyl”].



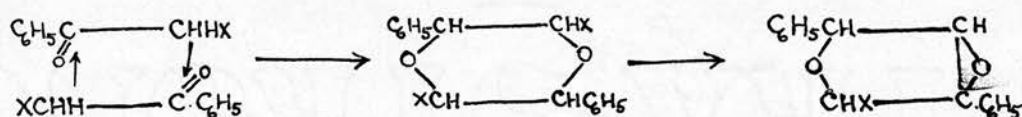
Trans—

[β -“halogendiphenacyl”].

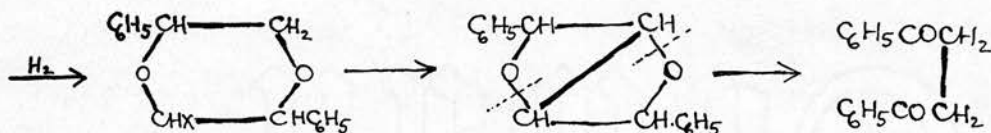
(X in the above configurations = halogen)

He assumed the reaction to take the following

course:



while the other stages are:

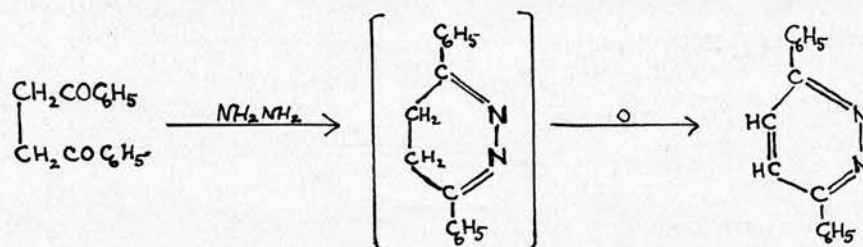


and with stronger reducing agents the keto groups were then attacked as well.

In the α - and β -halogendiphenacyls the halogen atoms have been assumed to be very strongly bound than in γ -halogendiphenacyl, (the latter being known to yield dibenzoyl ethylene), and according to Widman (loc.cit.) such a mechanism, as indicated above, explained most of the anomalies related with the α - and β -halogendiphenacyls like their inability to react with ketonic and hydroxyl reagents and so on.

Among the various reactions of diphenacyl an interesting one is that of hydrazine hydrate. Paal and /

and Dencks (Ber.,36,495) observed that 3-6 diphenyl dihydropyridazine is initially formed which is then oxidized by air to yield 3-6 diphenyl pyridazine - a substance obtained by treating dibenzoyl ethylene with hydrazine hydrate (Paal and Schulze - (Ber.33,3800,35,168)



This brings us back to dibenzoyl ethylenes and to a review of their cis-trans isomerism.

It is a well known fact that of the two stereoisomeric forms of dibenzoyl ethylene, the colourless modification is obtained by exposing a solution of the yellow isomer in appropriate solvents to sunlight while the reverse change is brought about by leaving in contact with a trace of iodine or by heating with HCl.

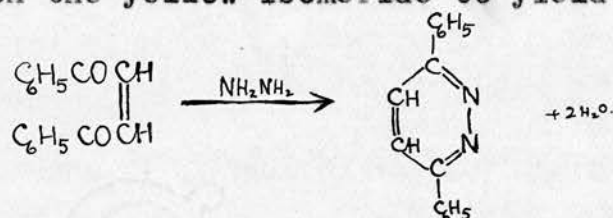
Paal and Schulze (loc.cit.) showed on a preparative basis that this arrangement proceeded quantitatively - a generalization confirmed later by Conant and Lutz (J.A.C.S.,1923,45,1303;1925,47,881) and by spectrographic means by Keller, Pasternack and v.Halban (Helv.Chim.Acta,1945,28,542;1946,29,512).

The configurations assigned to the unsaturated 1,4-diketones seem to be clearly established by all these workers.

Weygand/

Weygand and Lanzendorf (J.pr.Chem.1938,151,208) determined their dipole moments and found that for the colourless variety: $\mu = 3.36 \times 10^{-18}$ while for yellow, $\mu = 2.58 \times 10^{-18}$.

Attention here, will however be confined to the work of Paal and Schulze who assigned a cis-configuration to the high melting (colourless) isomer of dibenzoyl ethylene in view of its greater sensitivity towards hydrazine hydrate as compared with the yellow isomeride to yield 3,6 diphenyl



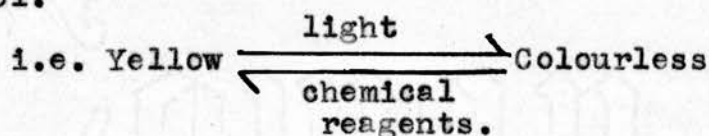
pyridazine, a conclusion supported later by Weygand and Lanzendorf (J.pr.Chem.1938,151,204), who found that under identical conditions the colourless isomers of various unsaturated 1,4-diketones react with hydrazine hydrate whereas the corresponding yellow isomers remain unreacted.

Miss Smedley (J.C.S.1909,95,219) on the basis of a determination of the refractive indices and the higher melting point of the colourless isomer, (of dibenzoyl ethylene), reversed Paal's configuration, but the validity of her argument was later challenged by other workers.

Conant and Lutz (loc.cit.) prepared other compounds of the same series and were able to show that except dibenzoyl ethylene, the colourless isomer in /

in all other cases had a lower melting point than its yellow isomeride.

A second consideration lies in the close analogy between the energy relationship of these cis-trans isomeric pairs, and that of maleic and fumaric acids (Stoermer, Ber. 42, 4870, (1909)) - the labile (or cis) isomer possessing a greater energy content being formed from the trans-isomer by the absorption of light energy; and rearranging under the influence of catalysts like a trace of iodine or by warming with HCl.



Lutz (J.A.C.S., 1930, 52, 3405, 3423) was able to confirm this evidence based on energy relationship by preparing unsaturated dibromo-1,4-diketones by the Friedel Crafts reaction on the trans-aroyle dibromo-acrylyl chlorides and on dibromofumaryl chlorides and thence determining their configuration.

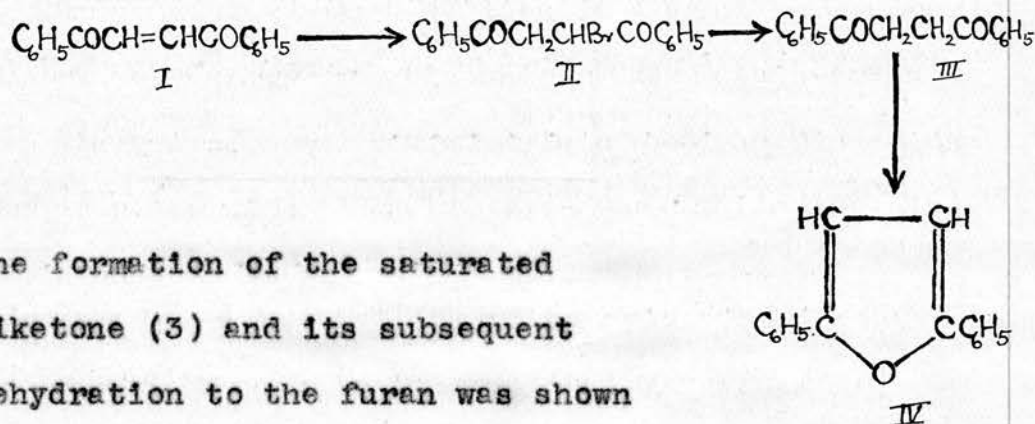
While ^{the} literature is replete with accounts regarding the mechanism of addition of halogens and halogen halides, surprisingly little information is available, for example, about the reaction between diphenacyl (1 mol.) and bromine (one or two mols.) to yield, α -brom- α - β diphenacyl or α - β -dibrom- α - β -dibenzoylethane, products which might be identical with those obtained by reacting dibenzoylethylenes in warm glacial acetic acid with HBr and a mol. of bromine respectively (Paal & Schulze - loc. cit.)

In /

In the latter case two dihalides ($\text{C}_6\text{H}_5\text{COCHXCHXCOC}_6\text{H}_5$) should be available and except in the addition of chlorine to cis and trans isomers of dibenzoylethylene, where both the dihalides were known (Conant and Lutz, J.A.C.S. 1925, 47, 881), only one dibromide was known prior to the work of Lutz (J.A.C.S., 1926, 48, 2905). It was then shown by him that the lower melting stereoisomeric dihalides are formed simultaneously in practically every case though only in small amounts. Bromine was next added nearly quantitatively (Lutz, J.A.C.S., 1927, 49, 1106) at -12°C to cis and trans dibenzoylethylenes in chloroform solution to give exclusively in the first case the lower melting (α -) and in the second case, higher melting (β) dibenzoyldibromoethane. Lutz further showed that the configurations of these dihalides corresponded to those of the halogen succinic acids from which they were obtained and according to him, the α -dichlorides were dl- and β -dichlorides - the meso.

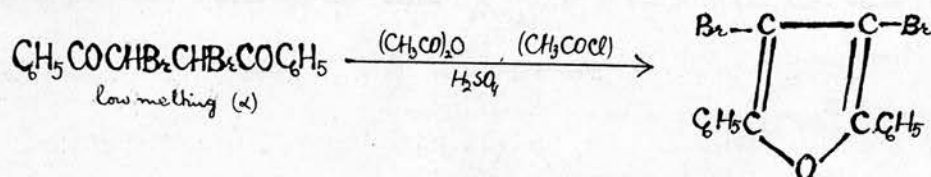
Lutz and Couper (J.Org.Chem. 1942, 7, 79) obtained another interesting result. They showed that if the reaction between HBr and dibenzoylethylene in glacial acetic acid was carried out in presence of β -naphthol and the mixture allowed to stand until further reaction beyond the initial addition had taken place, then 2,5 diphenylfuran and α -bromo- β -naphthol were obtained. The reaction disregarding equilibrations and intermediate steps being assumed to /

to proceed as follows:



The formation of the saturated diketone (3) and its subsequent dehydration to the furan was shown under the same experimental conditions in an independent experiment.

While furan formation is known to occur easily with both of the diastereoisomeric dibenzoyl-dichloroethanes, yet in the case of the two stereoisomeric dibromides (Lutz-J.A.C.S., 1926, 48, 2916,) after treatment with acetic anhydride and sulphuric acid, the α -form was found to react partially to give a low yield of the diphenyl dibromofurane, whereas the β -isomer, even after having been brought completely into solution by heating was found to remain unaffected. It was then concluded that the configuration possessed by the α -group of isomers was more favourable for ring closure of this type:

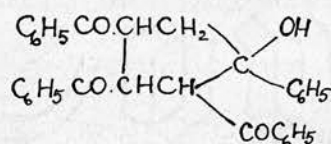


A mechanism - involving the 1,4-addition of the solvent-acetic anhydride or acetyl chloride and the loss of acetic /

acetic acid from the intermediate enol or acetic anhydride from an acetylated dienol.

Reduction has also been interpreted by a similar mechanism. The reduction of unsaturated 1,4-diketones in homogenous solution with soluble reducing agents leads exclusively to mono-molecular products - the saturated 1,4-diketones or the corresponding furans. The mechanism being assumed to involve 1,6-addition of hydrogen or their equivalents at the oxygen atoms at the end of the conjugated system.

Reductions with metal combinations, however, (Lutz, J.A.C.S. 1935, 57, 1953) presented another picture. It is an established fact that trans-dibenzoyl ethylene is reduced mainly to diphenacyl by zinc dust in hot glacial acetic acid. When this reduction is carried out in the cold a very large amount of dimolecular product (cyclo-bis-dibenzoylethane)



with a small amount of the monomolecular product, (diphenacyl) is formed.

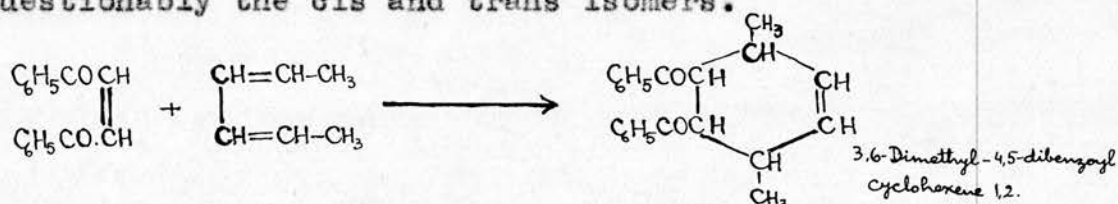
The catalytic hydrogenation of trans-dibenzoyl ethylene, also under different conditions has been found to result in both mono-and dimolecular products, while other unsaturated 1,4-diketones including cis-dibenzoylethylene and the halogen derivatives undergo largely monomolecular reduction. This /

This formation of cyclic dimolecular products was regarded by the same author as evidence that in reduction by zinc and glacial acetic acid or catalytic hydrogenation, conjugate addition was involved, and that direct addition of hydrogen to the ethylene linkage did not occur.

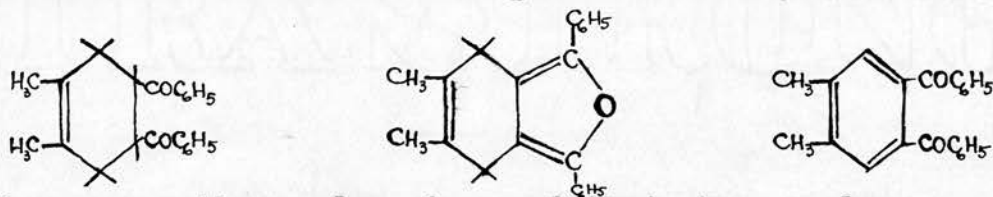
Earlier, the same author (J.A.C.S. 45, 1047 (1923)) had anticipated that in homogenous solution where the configuration was without any marked effect, both carbonyl groups of either cis or trans isomers which were surrounded by reductant ions, were supposed to react practically simultaneously, while in reduction with, say, a metal-combination the two carbonyl groups in the cis-compound could react almost simultaneously at the metal surface but in the trans compound, however, the reaction initiated at one carbonyl oxygen with the other spatially removed from the immediate source of hydrogen could hardly proceed so quickly and thereby affording a greater opportunity for ^{the} dimolecular reaction to become a dominant reaction.

The work of Conant, Lutz and co-workers (J.A.C.S., 1922, 44, 3802; 45, 1047, (1923); 46, 1254 (1924); 51, 3008 (1929); 49, 1036, (1926)) on the reduction of unsaturated 1,4-diketones revealed valuable information concerning reduction of such conjugated systems. By a series of planned experiments they showed that the first step in the process is the formation of a complex, that is a dienol which then undergoes /

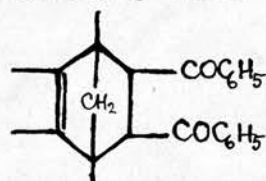
The Diels-Alder reaction between hexadiene -2:4 and trans-dibenzoyloethylene (Roger Adams and T.A. Geissmann, J.A.C.S., 1939, 61, 2083) yielded a mixture of two products (in 10:1 ratio) which were unquestionably the cis and trans isomers.



In a further systematic study on the diene addition products Roger Adams and Marvin H. Gold (J.A.C.S. 1940, 62, 56) found that butadiene and 2,3dimethyl butadiene condense with trans-dibenzoyloethylene to give 4,5 dibenzoylcyclohexene and its 1,2 dimethyl derivative. These dibenzoyl compounds can then be quantitatively converted by means of a few drops of sirupy phosphoric acid in acetic anhydride to dihydroisobenzofurans which in turn by bromine and sodium acetate give o-dibenzoylbenzenes.

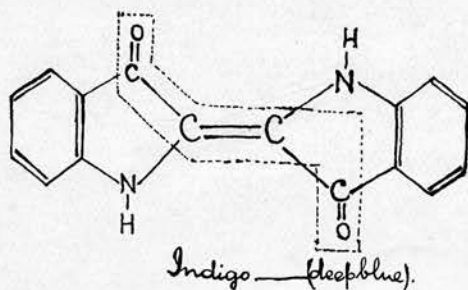


The same authors also observed that when cyclopentadiene was added to trans-dibenzoyloethylene, a compound presumably with the structure

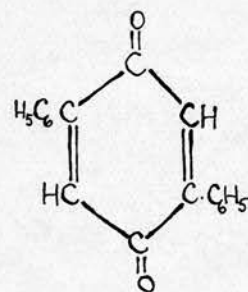


was produced.

This isomer as is obvious, represented a molecule in which the benzoyl groups were trans or on opposite /

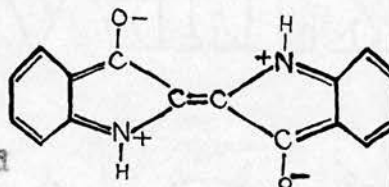


Abs. maxima in xylene = 5900Å



2,5-Diphenyl-1,4-benzoquinone
(Orange-yellow)

A completely satisfying configuration of the dyestuff has not yet been obtained though many attempts have been made to account for the anomalies in the structure of indigo, e.g. Kuhn's suggestion that indigo might be formulated as a trans-tetrapolar molecule and which has since then led to the generally accepted view that indigo should be regarded as a resonance hybrid of the Baeyer structure and Kuhn's quadripole.



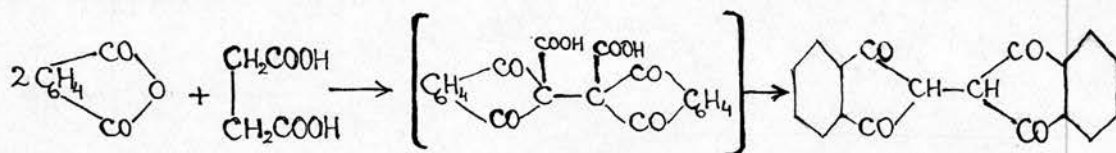
From what has been said above it seemed possible that the cis-form of indigo might lack the deep colour of the trans. The publication of Heller's work (Ber., 1939, 72, 1858), only recently available, shows that this is not the case; the cis-form having also a deep blue colour. Nevertheless it is of great interest to study the contrast in colour between cis and trans isomers as in the dibenzoyl ethylene series. It was, therefore, decided to prepare such compounds in which auxochromic groups like amino etc., are present.

In addition to the methods already discussed, mention may be made of the following:

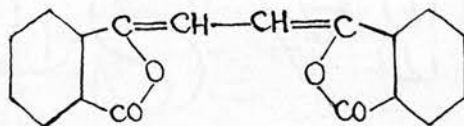
Gabriel and Leupold (Ber., 31, 1160) prepared ethinediphthalid /

ethinediphthalid by condensing phthalic anhydride and succinic acid in the presence of potassium acetate.

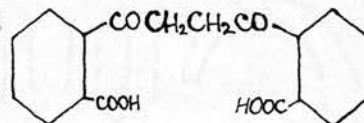
Some years earlier, Gabriel and Michael (Ber.10,1559) had obtained the same compound by using sodium acetate instead of potassium acetate and they regarded the resulting product as a diketohydrindene derivative:



Roser (Ber.,18,3115) showed that this was an unsaturated lactone and possessed the configuration:

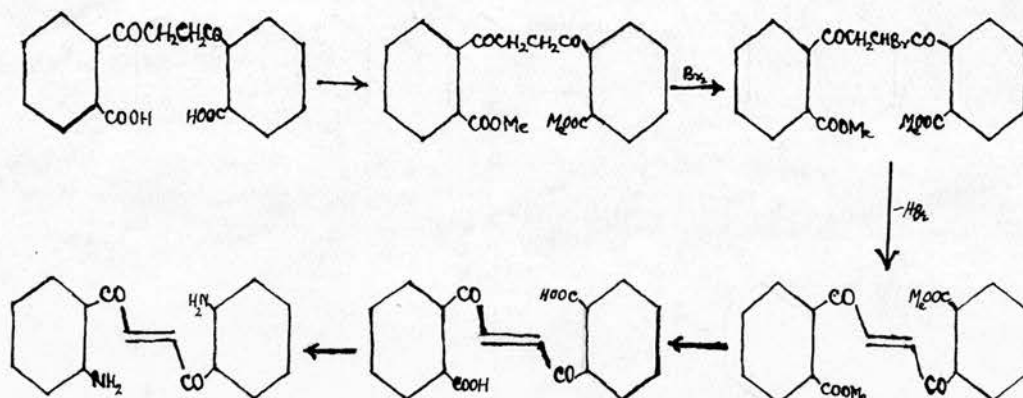


However, this compound on hydrolysis gave diphenacyldicarboxylic acid



From this compound the corresponding unsaturated derivative has not so far been obtained.

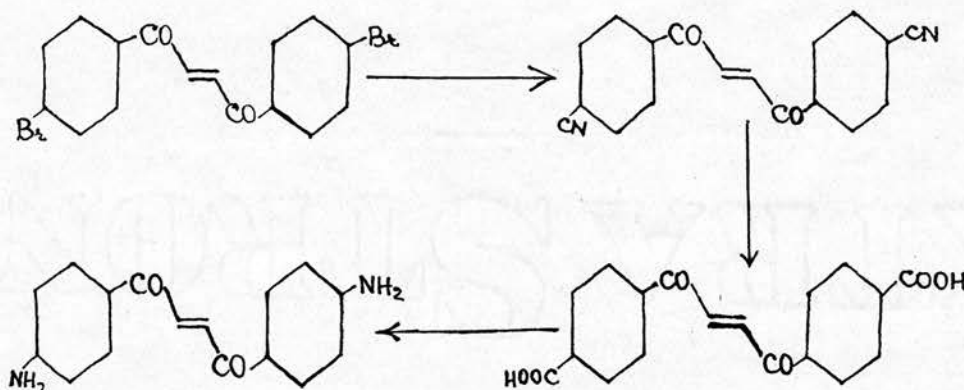
It was thought that the following plan might help in giving us some assistance:



Another feasible preparation was thought to be by way of preparing Dinitro-diphenacyls and through these the dinitrodibenzoylthylenes which could then be converted into the amino derivatives.

It should, however, be noted that the literature records no reference about the preparation of saturated or unsaturated γ -diketones by the Grignard reaction with either succino or fumaric nitriles respectively.

Yet another idea was to work as follows:



The reaction between dimethylaniline and fumarylchloride appears to be unknown so far, while no reference is available about the preparation of sym-di(o,meta,or paranitrobenzoyl)-ethylenes from 2 or 3 or 4-nitrophenacylbromides or chlorides and aq. KOH (cf. Bogoslovskii, loc. cit.), nor does any record about the reaction between 3- or 4-nitrophthalic anhydride and succinic acid in presence of sodium or potassium acetate exist.

OBJECT OF RESEARCH

The work described in the present thesis falls into the following sections:-

- (1) Preparation of the isomeric 1:2 dibenzoyl-ethylenes and their substituted derivatives by different methods and thence the attempted preparation of compounds comparable to indigo.
- (2) A study of their properties with particular reference to their cis-trans isomerism and the mechanism of their reduction.

EXPERIMENTAL SECTION.

The experimental work carried out is described in the following pages. Yields of products are quoted as percentages of the maximum theoretical amounts obtainable.

Melting points were determined on the apparatus described in "Qualitative Organic Chemistry" by Neil Campbell (p.7, fig. 4) and were checked for sharpness on a micro melting point apparatus (Kofler, Mikrochem, 1934,15,242).

All new compounds were analysed by Drs. Weiler and Strauss of Oxford.

-----oOo-----

PREPARATION OF PHENYLGLYOXAL:(Riley Org. Syntheses, 15,67.).

Selenium dioxide (40 g.) was dissolved in warm alcohol (200 cc.) and water (8 cc.). Acetophenone (41 g.) was added in one lot and the mixture heated over a water bath (temp. 50-55°C) for five hours with continuous stirring. The hot solution was separated from the precipitated selenium and the bulk of the excess of alcohol and water removed by distillation. The resulting yellow solution was then distilled under reduced pressure when phenylglyoxal came over at 95/101°C and 26.5 mms. pressure, as a yellow viscous oil.

Yield = 29.3 g. corresponding to 66%

The equation for the reaction is:



In a previous experiment where the pressure was not low, very poor yields of phenylglyoxal were obtained.

PREPARATION OF FUMARYL CHLORIDE:

Difficulty was encountered in the preparation of this reagent. Reaction with thionyl chloride yielded practically no acid chloride.

In the first experiment of this series, fumaric acid (5 g.) was heated with thionyl chloride (12 g.) for six hours. No acid chloride was /

was obtained as whole of the liquid distilled over at $75/78^{\circ}\text{C}$, leaving a white residue in the flask. The distillate was identified as thionyl chloride.

In the second trial, fumaric acid (5 gms.) and thionyl chloride (12 g.) were heated together for 18 hours, (cf. Meyer, Monatsch, 1901, 22, 415) Practically the whole of thionyl chloride was recovered on distillation and there was no sign of acid chloride being formed.

Fumaric acid (4 gms.) and thionyl chloride (11 g.) were next heated for 20 and 24 hours. In both these cases, practically all the thionyl chloride was recovered.

In another experiment fumaric acid (3 g.) and thionyl chloride (10 g.) were heated together in the presence of a very small amount of zinc chloride (<0.04 gms.). Still no fumaryl chloride could be obtained.

Maleic anhydride (5 gms.) and thionyl chloride (17 g.) were then heated together for twenty-four hours. No fumaryl chloride was formed as thionyl chloride was obtained leaving a white substance in the flask.

Maleic anhydride was obtained when maleic acid (5 gms.) and thionyl chloride (15 g.) were heated together for six and twelve hours.

In another attempt, thionyl chloride (5 gms.), maleic /

maleic acid (0.5 gms.) and a small drop of bromine were heated together under exposure to light from a 1000. watt lamp, for four hours. Distillation yielded thionyl chloride.

Phthalyl chloride (14 g. prepared according to Ott, (Org. Syntheses, 11,88) from phthalic anhydride, PCl_5 , AlCl_3 etc.) was cautiously mixed with fumaric acid (3.7 gms.), and after the liberation of HCl . ceased, the mixture was warmed and distilled. Only about a gm. of a colourless liquid (B.P.150/162°C.) was obtained. Since this procedure involved a long and laborious preparation, and the yield being very low, it was abandoned and fumaryl chloride eventually prepared from fumaric acid and phosphorous pentachloride (Kekulé, Annalen, Suppl.2,86., Von Auwers, Ber.,1913,46,480):

Fumaric acid (25 g.) and phosphorous pentachloride (100 g.) were heated together for half an hour over a water bath. The clear solution thus obtained was quickly decanted off and fractionally distilled. The fraction coming over at 130/160° being collected.

It was redistilled when 25.8 gms. of fumaryl chloride (B.P.153/160°C) were obtained: Yield = 77%.

In another experiment where a lesser amount of PCl_5 was used (fumaric acid (20 gms.) and PCl_5 (70g.)) a much smaller yield of fumaryl chloride was obtained: 11.2 gms. corresponding to 45%(app) of theoretical.

PREPARATION OF DIBENZOYL ETHYLENE:

(Conant and Lutz, J.A.C.S. 1923, 45, 1303)

Fumaryl Chloride (7 gms.) was added gradually to a well stirred mixture of benzene (100 c.c.) and aluminium chloride (20 gms.). The mixture was kept cool by external cooling. After the addition of the acid chloride, the reaction mixture which had set to a thick reddish paste was left at room temperature for an hour and decomposed by pouring it upon ice and letting it stand with water for half an hour. The yellow benzene layer was separated, washed with dilute Na_2CO_3 solution and water; dried over anhydrous sodium sulphate and the benzene evaporated. The resulting yellowish orange substance was crystallized from alcohol when pale yellow needles (m.p. $109/110^\circ\text{C}$) were obtained. The alcoholic mother liquor was boiled for half an hour with a little animal charcoal and after concentration of the solution, a second crop of pale yellow needles (m.p. $108/110^\circ\text{C}$) was obtained.

Yield: 7.1 gms.

65% of the theoretical.

The colourless isomer (needles) was obtained by exposing an alcoholic solution of the yellow isomer for two hours to bright sunlight. The conversion here was almost quantitative; (m.p. of the colourless needles - $133/134^\circ\text{C}$).

Preparation of Ditoluyyl Ethylene:

PREPARATION OF DITOLUYL ETHYLENE:

Toluene = 100 cc.

Aluminium Chloride = 20 g.

Fumaryl Chloride = 10 g.

The Friedel-Craft's reaction was carried out as before and 9.2 g. of the yellow isomer were obtained after two crystallizations from alcohol. (m.p. 145/147°C). Yield = 52% of the Theoretical.

The colourless isomer (m.p. 123°C) was obtained by exposing to bright sunlight for six hours an acetone solution of the yellow isomer placed in a quartz test-tube. Yield: Nearly quantitative.

Di(p-Chlorobenzoyl)-Ethylene:

In a similar Friedel-Craft's synthesis, fumaryl chloride (8 g.) was added to a well stirred mixture of chlorobenzene (20 g.) diluted with carbon disulphide (50 cc.) and anhydrous aluminium chloride (22 g.). Half an hour after the addition of the acid chloride, the reaction mixture was heated to 40-45°C. over a water bath for two hours and decomposed as usual by pouring it on to crushed ice. After extraction with the addition of a little chloroform, and washing well with water, the carbon disulphide and chloroform were evaporated and the resulting orange yellow resinous product triturated with light petroleum (100/120°C.) and the yellow solid crystallized from a mixture of alcohol and acetone when 8.1 g. of pale yellow needles (m.p. 171/172°C) /

(m.p. 171/172°C) were obtained.

m.p. quoted in literature = 172°C.

Yield = 51% of Theoretical.

The colourless isomer was obtained in quantitative yields by exposing a chloroform solution of the yellow isomer to bright sunlight for six hours, in a quartz test-tube. Colourless needles - m.p. 101/102°C. after crystallization from alcohol.

Di(p-Bromobenzoyl)Ethylene:

(Conant and Lutz - J.A.C.S. 1925, 47, 881)

As in previous cases, fumaryl chloride (10 g.) was added gradually to a well stirred mixture of bromobenzene (23 g.) anhydrous aluminium chloride (21 g.) and carbon disulphide (50 cc.). An hour after the addition of the acid chloride, the reaction mixture was warmed to 40-45°C over a water bath for half an hour and then decomposed by pouring it on to crushed ice. Extraction with chloroform, followed by washing with dilute Na_2CO_3 solution and water and subsequent evaporation of the chloroform and carbon disulphide resulted in a yellowish orange oily product which was triturated with light petroleum and crystallized from chloroform and acetone. 10.8 g. of pale yellow leaflets (m.p. 186/188°C.) were obtained.

Yield = 42% of the Theoretical.

The colourless isomer was obtained in quantitative /

quantitative yields by exposing a chloroform solution of the yellow isomer to bright sunlight for six hours in a quartz tube. Colourless needles - m.p. 123°C.

In all these cases the conversion of the trans into cis forms was never complete when their solutions in suitable solvents placed in quartz vessels were exposed to ~~the~~ the Ultraviolet light and light from a 1000 watt lamp.

Preparation of p-Bromobenzoylformaldehyde:

p-Bromoacetophenone (20 g.) was added to SeO_2 (11.2 g.) dissolved in 95% alcohol (70 cc.) and water (8 cc.). The mixture was heated (at 70°C) on a water bath, with frequent shaking, for six hours. It was filtered and as much of alcohol and water as possible distilled off. The residual orange coloured liquid was then distilled under reduced pressure when 12.3 g. of an orange red oil (B.P. 135/142°C at 17 mms.) were obtained.

Yield = 58% approximately.

The equation for the reaction is:



*monohydrate
mp. 132-133°.
Kameli & Kinsman,
Helv., 1935, 18, 1140
mp. 125°.*

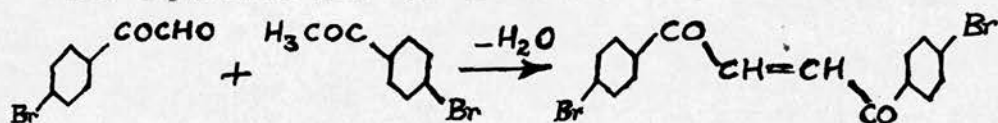
Preparation of Di(p-bromobenzoyl)Ethylene:

(Cf: Weygand and Lenzendorf, J.pr.Chem. 151, 205, (1938))

p-bromobenzoylformaldehyde (7 g.) with p-bromoacetophenone (6.8 g.) and 20 cc. glacial acetic acid and a drop of concentrated H_2SO_4 were refluxed for an hour and a half. It was cooled and /

and poured into 100 cc. of cold water, and the yellowish orange precipitate extracted with chloroform. The dried chloroform solution was evaporated and the yellowish orange residue recrystallized from chloroform. 3.81 g. of pale yellow leaflets (m.p. $187^{\circ}\text{C}.$) were obtained. Mixed m.p. with an authentic sample (of yellow isomer of Di(p-bromobenzoyl)-Ethylene prepared according to Conant and Lutz (J.A.C.S. 1925, 47, 891)) showed no depression. m.m.p. = $187/188^{\circ}\text{C}.$

The equation for the reaction is:

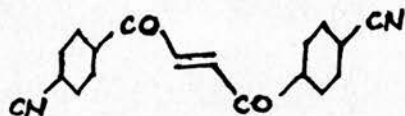


The colourless isomer, (no reference in the literature), was obtained by exposing one gram of the yellow isomer of Di(p-bromobenzoyl)Ethylene in chloroform solution (30 cc.) to bright sunlight for six hours. The colourless solution thus obtained was evaporated to dryness and the white residue recrystallized from ligroin. (m.p. = $123^{\circ}\text{C}.$)

Analysis	-----Found-----	Theoretical for
		$\text{C}_{16}\text{H}_{10}\text{O}_2\text{Br}_2$
Bromine40.26%-----	40.5%

Attempted preparation of Di(p-bromobenzoyl) Ethylene according to the method of Smedley (J.C.S. 95, 219). p-Bromobenzoylformaldehyde (1.45 g.) and p-bromoacetophenone (1.35 g.) with 20 cc. of acetic anhydride were refluxed for one hour, cooled and poured into 100 cc. of cold water when an orange-yellow oily liquid was obtained. It could not be purified.

Attempted Preparation of Di(p-Cyanobenzoyl)Ethylene:



(cf. preparation of α -naphthonitrile Newman, Org. Syntheses, Vol. 21, 89)

(1) Di(p-bromobenzoyl)ethylene (4 g. of the yellow isomer), with about the same quantity of pure dry cuprous cyanide and dry pyridine (20 cc.) was heated for sixteen hours at 190°C - 195°C. The resulting dark brown solution, while still hot (about 100°C) was poured into aq. ammonia (50 cc.) and water (50 cc.), benzene (60 cc.) was added and the mixture shaken well. After cooling it (to about 30°C), ether (50 cc.) was added and the mixture filtered through a sintered glass funnel. The ether-benzene layer was separated and washed several times with dilute aq. NH_4OH till the final ammoniacal washing was colourless. After being well washed with 6-N-HCl and water, the ether-benzene solution was dried over anhydrous Na_2SO_4 , and from the yellow-brown solution, ether and benzene were removed by distillation when a yellowish brown substance was obtained (m.p. 130/137°C.) All attempts to obtain anything crystalline out of it were unsuccessful (the substance is fairly soluble in benzene and alcohol etc.)

(11) Di(p-chlorobenzoyl)ethylene, (yellow isomer) was used in another experiment instead of Di(p-bromobenzoyl)ethylene, and, working in a similar manner, but this time heating for 24 hours, a brownish yellow resinous product was obtained. Trituration with light petroleum followed by attempted crystallizations from a mixture of benzene and light petroleum resulted only in giving a dirty yellowish brown substance which also melted over a wide range (127/135°C). Further purification was not possible, so this substance was not investigated any more.

Attempted Preparation of di(p-dimethylamino benzoyl)ethylene.

Dimethylaniline and fumaryl chloride.

Dimethylaniline (20 g.) obtained pure by fractionally distilling the amine (25 g.) with a little acetic anhydride (3-4 cc.) was treated with fumaryl chloride (6.5 g.) in the presence of benzene (70 cc.). The mixture was left for twenty hours at ordinary room temperature after which it was slightly warmed by placing on a water bath and then treated with dilute Na_2CO_3 solution, when /

151 - 172

trans - di (p-chloro) + ethane = 154-156
softening at 159/160

cis - di (p-chloro) + ethane = 129/131°C

~~softens~~ ^{melts} at 96/99° — mmp = ~~116/118°C~~ 111

trans - Di (p-bromo) + ethane = 182/183°C.

cis — about 125/130°

trans - Dibenzyl ethylene + ethane = 146/148°C

cis — " " + ethane = 116/118°C

when a black resinous product was obtained. It was separated, washed well with water, treated with acetone and filtered. The residue on the filter was almost black while the filtrate possessed a violet tinge. The residue on the filter was insoluble in hot alcohol and benzene but dissolved (giving almost a black solution) in hot glacial acetic acid, and on cooling, a black precipitate was obtained after diluting with a little water. This was not investigated further, nor was the dark brownish violet acetone solution.

The Friedel-Crafts reaction between Anisole, fumaryl chloride in presence of aluminium chloride and nitrobenzene as a diluent, gave a dark brown tarry product which could not be purified either.

Reaction with Hydrazine Hydrate:

In all the following reactions, a solution of hydrazine Hydrate (50% W/W) was used.

Dibenzoyl Ethylene:

(a) The colourless isomer (0.10 g.) dissolved in alcohol (10 cc.) was treated with hydrazine hydrate solution (0.5 cc.), left overnight at room temperature, filtered and dried. Needle-like crystals, m.p. 226°C . of 3:6-diphenylpyridazine were obtained.

Analysis:	Found	Theoretical for $\text{C}_{16}\text{H}_{12}\text{N}_2$
Nitrogen	11.8%	12.07%

(b) The yellow isomer (0.1 g.) dissolved in alcohol (10 cc.) was treated with hydrazine hydrate (0.5 cc.) left overnight at room temperature and the yellow leaflets separated (m.p. $146/147^{\circ}\text{C}$).

Analysis:	Found	Theoretical
Nitrogen.	11.3%	11.2% (corresponding to $\text{C}_{16}\text{H}_{14}\text{ON}_2$, i.e. a monohydrazone).

The analysis corresponds to that of dibenzoyl ethylene monohydrazone.

This yellow substance (m.p. $146/147^{\circ}\text{C}$) was dissolved in the minimum amount of glacial acetic acid and the solution heated. The yellow solution soon became colourless and on cooling, colourless needles were obtained (m.p. $225/226^{\circ}\text{C}$). Mixed m.p. with 3:6 diphenylpyridazine (obtained before), gave no depression (m.m.p. = $224/226^{\circ}\text{C}$).

-59-

Ditoluylethylene:

(a) The colourless isomer (0.10 g.) dissolved in alcohol (15 cc.) was treated with hydrazine hydrate solution (0.5 cc.) left overnight and the colourless needles of 3:6-ditoluylpyridazine thus obtained were recrystallized from alcohol (m.p. 231/232°C).

Analysis	Found	Theoretical ($C_{18}H_{16}N_2$)
Nitrogen	10.15%	10.7%

(b) The yellow isomer (0.11 g.) likewise, dissolved in alcohol (15 cc.) was treated with hydrazine hydrate (0.5 cc.), left overnight but nothing separated out. A little alcohol was evaporated when a yellow gummy mass separated out. Its crystallization from alcohol gave pale yellow needles (m.p. 144/146°C). Mixed m.p. with the yellow isomer of Ditoluylethylene gave no depression (m.m.p. = 145/148°C.) From the mother liquor, evaporation of some more alcohol yielded a little more yellow gummy mass, which was also crystallized from alcohol (pale yellow needles - m.p. 144/145°C. - no depression in mixed m.p., which was 144/147°C).

(c) Ditoluylethane (0.1 g.) dissolved in alcohol (12 cc.) also treated with hydrazine hydrate (0.5 cc.). A white crystalline precipitate separated (m.p. 177/178°C). The solution, after being left overnight, was filtered when colourless needles /

needles (M.P. 230/231°C) were obtained. Mixed m.p. with the product obtained from the colourless isomer of Ditolylethylene gave no depression (m.m.p. = 230/232°C).

NOTE: In the following experiments, glacial acetic acid was used instead of alcohol as the yellow isomers of Di(p-chlorobenzoyl) and Di(p-bromobenzoyl)Ethylenes are sparingly soluble in alcohol.

Di(p-Chlorobenzoyl)-Ethylene:

(a) The colourless isomer (0.11 g.) dissolved in glacial acetic acid (11 cc.) was treated with hydrazine hydrate (0.5 cc.). Leaving overnight gave colourless needles - (m.p. 264°C) of 3:6 - di(p-Chlorophenyl)-pyridazine.

Analysis	Found	Theoretical for $C_{16}H_{10}N_2Cl_2$
Nitrogen	9.7%	9.3%

(b) The yellow isomer (0.11 g.) dissolved in glacial acetic acid (11 cc.) likewise treated with hydrazine hydrate (0.5 cc.). The solution was left overnight and the yellow precipitate filtered and dried (m.p. 170/171°C). A mixed m.p. with the yellow isomer of Di(p-Chlorobenzoyl)-Ethylene gave no depression (m.m.p. = 170°C.).

(c) The yellow isomer (0.107 g.) dissolved in glacial acetic acid (10 cc.) treated with hydrazine hydrate solution (0.5 cc.) and the solution heated almost to boiling for four to five minutes. The original pale yellow solution became colourless /

colourless and on cooling deposited a white substance (m.p. $260/263^{\circ}\text{C}$). Recrystallization from alcohol gave colourless needles m.p. $262/264^{\circ}\text{C}$. Mixed m.p. with the product obtained from the colourless isomer gave no depression as the mixture melted at $262/264^{\circ}\text{C}$.

Di(p-bromobenzoyl)-Ethylene:

Both the isomers were worked up in the same way as Di(p-chlorobenzoyl)-Ethylene. The colourless isomer yielded a product melting at 285°C , while under similar conditions the yellow isomer was obtained unreacted but the yellow isomer (as in the case of the chloro compound) reacted with NH_2NH_2 when the glacial acetic acid solution was heated (to boiling) for five minutes, and the resulting compound was identical with that obtained from the colourless isomer.

The analysis was, however, faulty:

Found	Theoretical for $\text{C}_{16}\text{H}_{10}\text{N}_2\text{Br}_2$ (i.e. 3:6 -
	di(p-bromophenyl)-pyridazine.
Nitrogen 5.44%	7.18%

This may be attributed to the substance being impure.

Reduction with Aluminium Isopropoxide:

As recommended in "Organic Reactions", Vol.II, (Wiley-New York 1944 p.190) the following general procedure was employed for all the reductions with this reagent.

In a small round bottomed flask (50 cc.) fitted with a modified type of Hahn partial condenser were placed the reactants and the mixture heated on a water bath (80-90°C). The time required in each experiment is reported in individual cases below. Acetone along with isopropyl alcohol distilled over and sometimes it was necessary to add a little more isopropyl alcohol in order to take the reaction to completion. When acetone test became negative as indicated by 2:4-dinitrophenylhydrazine reagent, heating was stopped, isopropyl alcohol distilled under reduced pressure and the residue treated with HCl (conc.HCl diluted with three times its amount of water). The resulting product was then worked up as described below.

Dibenzoyl ethylene:

a i. Colourless isomer = 0.9 g.
Aluminium isopropoxide = 0.3 g.
Isopropyl alcohol = 20 cc.

The mixture was heated for four hours, and the white precipitate obtained after treatment with dilute HCl was crystallized from methanol and light petroleum /

petroleum, when a colourless crystalline substance (m.p. 147/150°C corr.) was obtained. It gave no indication of the presence of a double bond (Br_2), nor was it enolic (FeCl_3). It was insoluble in aq. NaOH solution but dissolved in concentrated sulphuric acid and the solution was red which turned green on being heated. The substance was recovered unchanged after treatment with acetic anhydride and a trace of concentrated sulphuric acid, but with PCl_5 there was effervescence.

Analysis gave: C = 71.16% and H = 5.16% which corresponds to neither a dienol nor diphenacyl (for which C = 80.67% and H = 5.8%). Gave a depression with diphenacyl (m.m.p. 126/128°C).

a. 11.

The experiment was suspected to be faulty and was repeated. The colourless isomer (0.8 g.), aluminium isopropoxide (0.35 g.) and isopropyl alcohol (30 cc.) were then heated for five and a half hours. The white precipitate obtained after treatment with HCl was crystallized from methyl alcohol (m.p. 143/147°C uncorr.) It was next dissolved in benzene and put through an aluminium column (14" x $\frac{1}{2}$ "). Developing with the same solvent gave the following fractions -

- a. A colourless product m.p. 140/142°C and its mixed m.p. with diphenacyl = 138/141°C.
(Yield about 0.1 g.)

b /

- b. 0.36 g. of colourless crystals which were crystallized from alcohol (m.p. 140/142°). Its mixed m.p. with diphenacyl gave no appreciable depression as the mixture melted at 138/139°C.

From the alumina column it was difficult to obtain any other product.

The experiment was repeated once again. The colourless isomer of dibenzoyl ethylene (0.52 g.), aluminium isopropoxide (0.36 g.) and isopropyl alcohol (45 cc.) were heated together for seven and a half hours under the same conditions as before. Diphenacyl (0.32 g.) was obtained, after being purified by chromatographic adsorption. The rest of the substance could not be investigated.

- b. Yellow isomer = 0.88g.
 Aluminium isopropoxide = 0.36g.
 Isopropyl alcohol = 28 cc. (20cc. initial
 plus 8cc. added later)

Heated under identical conditions as before, for six and a half hours. The yellow precipitate obtained after treatment with dilute HCl was crystallized from alcohol. There appeared to be a mixture of two substances as the solution was left overnight, one being pale yellow and the other almost colourless (m.p. 105/114°C).

The whole solution was then evaporated to dryness and next dissolved in benzene and chromatographed on an alumina column (16" x $\frac{1}{2}$ ").
 Developing /

b (Contd.).

Developing with the same solvent yielded two essential products:

1. Colourless crystals (needles) which were recrystallized from methylalcohol (m.p. 139/141°C). Mixed melting point with diphenacyl gave no depression (m.m.p. = 139/142°C). Yield = 0.61 g.

ii. Pale yellow needles m.p. 101/102°C.

After trituration with light petroleum and recrystallization from alcohol, they melted at 106/108°C. A mixed m.p. with the yellow isomer of dibenzoylethylene gave no depression (m.m.p. = 106/109°C).
Yield about 0.05 g.

An intermediate fraction, on evaporation of benzene and subsequent trituration with light petroleum gave about 0.1 g. of a pale yellow substance (m.p. 109/118°C) and was probably the yellow isomer contaminated with a little diphenacyl. The last fraction obtained after washing the column with a mixture of Benzene and alcohol (4:1 ratio), gave a yellowish oily liquid which was triturated with light petroleum and the pale yellow substance thus obtained melted at 96/99°C. Lack of material prevented its investigation. Probably it was unreacted yellow Dibenzoylethylene.

Ditoluylethylene:

a. Colourless isomer = 0.71 g.

Aluminium isopropoxide = 0.36 g.

Isopropyl alcohol = 25 cc.

Heated for five hours, and the colourless substance obtained after treatment with HCl was dissolved in benzene and put through a short alumina column (6" x $\frac{1}{2}$ "). The colourless developed solution on evaporation gave a white product which was crystallized from alcohol when colourless needles (m.p. 156/157°C) were obtained. Recrystallization from methyl alcohol gave a better product (m.p. 157/158°C). A mixed m.p. with a genuine sample of 4-4' dimethyldiphenacyl gave no depression (m.m.p. = 156/158°C).

Yield = 0.67 g. of the reduced product.

Further confirmation about the formation of 4-4' dimethyldiphenacyl was obtained by treating the reduced product (0.1 g.) with bromine (0.02 cc.) in hot glacial acetic acid (5 cc.) and the α -brom - α - β -ditoluylethane thus obtained was next heated with quinoline at 170/175°C for twenty minutes. The reaction mixture was poured in dilute HCl (25 cc.) and the yellow precipitate crystallized from alcohol when pale yellow crystals were obtained (m.p. 145/146°C). It gave no depression in mixed m.p. with a sample of the yellow isomer of /

of ditoluyethylene, prepared according to Conant and Lutz (m.m.p. = 145/147°C).

- b. Yellow isomer = 0.77 g.
 Aluminium isopropoxide = 0.38 g.
 Isopropylalcohol = 35 cc. (25 cc. initial plus 10 cc. added later).

Heated for six and a half hours, and worked up as before. The pale yellow substance obtained after treatment with HCl was dissolved in benzene and chromatographed on an alumina column (18" x $\frac{1}{8}$ "). Three fractions were obtained:

1. Colourless solution which gave 0.57 g. of colourless needles (m.p. 155/157°C).

These were identified as 4-4' dimethyldiphenyl acyl by a mixed m.p. (156/158°C) with a genuine sample of the latter

11.0.08 g. of a yellow substance. Recrystallization from alcohol gave yellow needle-like crystals, m.p. 145/146°C. Mixed m.p. with the yellow isomer of ditoluyethylene gave no depression (m.m.p. = 144/146°C).

111. Another pale yellow solution which on evaporation yielded a yellow oily substance. Trituration with methyl alcohol preceeded by light petroleum, yielded a yellow substance which was recrystallized from methyl alcohol. (m.p. and m.m.p. with a sample of yellow ditoluyethylene = 144/147°C.)

Di(p-Chlorobenzoyl)Ethylene:

- a. Colourless isomer = 0.37 g.
Aluminium isopropoxide = 0.2 g.
Isopropyl alcohol = 20 cc.

Heated as usual for four hours and the white precipitate (m.p. 146/149°C) obtained after treatment with dilute HCl was dissolved in benzene and purified by putting it through an alumina column (8" x $\frac{1}{8}$ "). The colourless developed solution on evaporation gave 0.33 g. of a colourless substance which was crystallized from methyl alcohol (m.p. 148/149°C). A mixed m.p. with 4-4' Dichlorodiphenacyl gave no appreciable depression (m.m.p. = 146/149°C).

- b. Yellow isomer = 0.46 g.
Aluminium isopropoxide = 0.24 g.
Isopropyl alcohol = 30 cc. (20 cc.
initial plus 10 cc.
added later)

Heated for six and a half hours, and after working up in the usual manner, the pale yellow precipitate was treated with benzene. About 0.05 - 0.1 g. of a yellow substance did not dissolve. (m.p. of this substance = 169/171°C). This was identified later as the yellow isomer of di(p-chlorobenzoyl)ethylene (m.m.p. = 170/171°C).

The benzene solution was chromatographed on an /

b. contd.-

an alumina column (16" x $\frac{1}{8}$ ") when two products were obtained.

1. The colourless solution gave on evaporation a colourless product which was crystallized from alcohol when colourless needles, m.p. 148/150°C were obtained. Mixed m.p. with 4-4' dichlorodiphenacyl gave no depression (m.m.p. = 148/149°C). Yield = 0.3 g.

11. A faintly yellow solution obtained by developing with benzene and alcohol mixture (4:1). Evaporation to dryness gave a yellow oily substance which was triturated with methyl alcohol and the pale yellow substance thus obtained was recrystallized from alcohol (m.p. 169/171°C), mixed m.p. with di(p-chlorobenzoyl)ethylene gave no depression (m.m.p. = 170/172°C).

Di(p-bromobenzoyl)ethylene:

a. Colourless isomer = 0.18 g.
 Aluminium isopropoxide = 0.09 g.
 Isopropyl alcohol = 20 cc. (10 cc. initial
 plus 10 cc.
 added later.)

Heated /

a Contd.-

Heated for five hours under the usual conditions. The white precipitate obtained after treatment with HCl was dissolved in chloroform and purified by putting it through a short alumina column (8" x $\frac{1}{2}$ "). Evaporation of chloroform from the colourless developed solution gave 0.16 g. of colourless plate-like crystals (m.p. 174/176°C). Recrystallization from hot alcohol and glacial acetic acid yielded a purer product (m.p. 180/182°C). This gave no depression in mixed melting point with a sample of 4-4' dibromdiphenacyl (m.m.p. = 180/181°C).

b. Yellow isomer = 0.45 g.
 Aluminium isopropoxide = 0.21 g.
 Isopropyl alcohol = 20 cc.

The mixture was heated for seven hours and worked up in the usual manner. The yellow precipitate was dissolved in chloroform and chromatographed whereby 0.26 g. of pale yellow plates m.p. 184/186°C. were obtained. Since a very small amount (0.05 - 0.1 g.) of a colourless substance (m.p. 175/177°C) was isolated it was thought /

b Contd.-

thought advisable to repeat the experiment.

In this experiment eight and a half hours' heating of the yellow isomer of di(p-bromobenzoyl)ethylene (0.39 g.), aluminium isopropoxide (0.23 g.) and isopropyl alcohol (30 cc.) gave a yellow precipitate, which was dissolved in chloroform and chromatographed on an alumina column (18" x $\frac{1}{2}$ "). Two products were isolated.

1. 0.3 g. of a colourless substance
m.p. 179/180°C. Mixed m.p. with 4-4' dibromodiphenacyl gave no depression (179/181°C).
2. 0.05 (app.) g. of a pale yellow substance (m.p. 185/186°C). This was found to be the di(p-bromobenzoyl)ethylene by a mixed m.p. which was 185/186°C.

Preparation of saturated 1,4-diketones:

Succinyl Chloride (B.P. 191°C and m.p. 19/20°C) was obtained from succinic acid and phosphorous pentachloride.

a./

a. Diphenacyl, 4-4' Dimethyl Diphenacyl (see Hale and Thorp, J.A.C.S., 35, 265), 4-4' dibromdiphenacyl etc. were obtained by the Friedel Crafts' reaction with succinyl chloride. An hour after the addition of powdered AlCl_3 to the reactants, the mixture was warmed to about 55°C , left overnight and decomposed by pouring it over ice. Washing with water and removal of bromobenzene or toluene by steam distillation gave a dark coloured residue which was washed with a slight excess of 2% NaOH solution (about 50 cc.) whereby the lactone present and any other foreign matter could be easily removed. After filtration, the residue was washed well with water and recrystallized.

Yields were poor owing to the fact that the greater part of the acid chloride reacts in unsymmetrical form.

b. 4-4' Dimethoxydiphenacyl was prepared according to Borsche, (Annalen, 1936, 526, 19): To a stirred and well cooled mixture of anisole (60 g.), succinyl chloride (45 g.) and CS_2 (350 cc.), were gradually added 55 g. of finely powdered AlCl_3 . The product was kept at room temperature for 40 hours and was then decomposed by pouring on to crushed ice. CS_2 and unreacted anisole were removed by steam distillation, and the /

b. (contd.)

the residue taken up in ether, washed with 2N- Na_2CO_3 solution^{and} ether evaporated. The residue was further treated with 50 cc. of 20% K_2CO_3 and extraction with ether renewed. Evaporation of ether gave a pale yellow crystalline mass which was recrystallized from methanol when colourless needles m.p. 108/109°C were obtained.

Attempted preparation of 4-4'

Dimethoxydiphenacyl by the Friedel Crafts' reaction between anisole, succinyl chloride and AlCl_3 , with nitrobenzene as a diluent (instead of CS_2) and washing with 2% NaOH solution failed to give any successful result. A dark resinous produce was obtained instead.

Preparation of Diphenacyl:

Phenacylbromide (20 g.) dissolved in absolute alcohol (100 cc.) and cooled by means of a freezing mixture was treated with a cold solution of sodium (1.2 g.) dissolved in absolute alcohol (25 g.). The addition was made /

made gradually and the temperature maintained at -5°C throughout. After an hour, the reaction mixture was poured into water (300 cc.) and bromdiphenacyl filtered off and dried. Yield = 9.5 g. corresponding to about 60% of theoretical.

This monobromoderivative (4.8 g.) was next dissolved in 95% alcohol (250 cc.) and after the addition of magnesium powder (12 to 15 g.), was boiled under reflux for three hours, filtered and concentrated to less than a third of its original volume, when on cooling colourless crystals separated out from the faintly yellow solution. Recrystallization from alcohol gave 2.43 g. of colourless crystals (needles - m.p. $142/143^{\circ}\text{C}$) which showed no depression in mixed m.p. with a genuine sample of diphenacyl (m.m.p. = $142/144^{\circ}\text{C}$) Yield = 68%.

In previous experiments, reduction to diphenacyl did not proceed when magnesium turnings and aluminium powder were employed instead of magnesium powder. Yields with zinc dust were found to be low (about 38%) when the mixture was refluxed for two hours.

Phenacylbromide and aqueous KOH solution:

(Ajello Gazz. Chim. Ital. 1937, 67, 708., C.A. 1938, 32, 4566.)

Aq. KOH (6.5 g. in 15 cc. of water) was added extremely slowly over an hour, to phenacylbromide (30 g.) dissolved in 95% alcohol (100 cc.). The mixture was kept cool by an ice salt bath and vigorously stirred throughout by means of a mechanical stirrer. After the addition of the alkali, the mixture was let stand for two hours, diluted with water (25 cc.) and left overnight. The white precipitate was filtered washed with cold and hot water and alcohol (m.p. 131/134°C).

A small portion of it when recrystallized from aq. alcohol melted at 135/138°C.

Separation into the various components:

It is an established fact that α and β bromdiphenacyls differ from each other with regard to their solubility in benzene. On this basis a fractional crystallization from benzene, of Ajello's product, yielded two products:
(I) Melting at 157/158°C and (II) Melting at 130/132°C.

These are obviously β and α varieties of bromdiphenacyl.

γ -Bromdiphenacyl and reduction with magnesium powder:

γ -Bromdiphenacyl (0.96 g. obtained from diphenacyl (1mol) plus /

plus bromine (1mol) (~~0.75g~~ dissolved in 95% alcohol (50 cc.) were refluxed for four hours with magnesium powder (3 g.). As usual, after filtration and subsequent concentration, colourless needles (m.p. 141/143°C) separated out, which were identified as diphenacyl, (mixed m.p. with γ -bromdiphenacyl gave a depression (118/121°C) while with diphenacyl, m.m.p. = 142/144°C) Yield: = 0.65g.

γ -Bromdimethyldiphenacyl and reduction with magnesium powder:

α -Brom - α - β - ditoluyethane (0.75g) dissolved in alcohol (40 cc.) were, with 2 to 3 g. of magnesium powder, heated under reflux for four and a half hours. Filtered, concentrated to one third its original volume and allowed to crystallize out. Colourless needles (m.p. 156/157°C) were obtained which were recrystallized from alcohol (m.p. 157/158°C). A mixed m.p. with 4-4' dimethyldiphenacyl gave no depression as the mixture melted at 157/159°C.

Yield?

Diphenacyl and selenium dioxide:

Diphenacyl (1.7 g.) and SeO₂ (0.8 g.) dissolved in 95% alcohol (25 cc.) and water (1 cc.) /

(1 cc.) were heated under reflux for 24 hours. The pale yellow solution was separated from the precipitated selenium metal, and concentrated to half its volume. On cooling, pale yellow needles (m.p. 107/109°C) were obtained. Recrystallized from alcohol (m.p. 109/110°C). A mixed m.p. with a sample of the yellow variety of dibenzoyl ethylene, prepared according to Conant and Lutz (J.A.C.S. 1923, 45, 1303), gave no depression (m.m.p. = 108/110°C).
Yield = 0.96 g. corresponding to 56%

In a second attempt, diphenacyl (1.2 g.) and SeO_2 (0.57 g.) were heated for sixteen hours in 95% alcohol (20 cc.), water (1 cc.) and a drop of HCl. Worked up in a similar manner as above when pale yellow needles of dibenzoyl ethylene (0.88 g.) were obtained, (identified by m.p. and mixed m.p. which were both 108/110°C).
Yield = 73%.

4-4' Dimethyldiphenacyl and selenium dioxide:

- (1) 4-4' Dimethyldiphenacyl (1.67 g.) and SeO_2 (0.71 g.) dissolved in 95% alcohol (25 cc.) and water (1 cc.) were refluxed for 72 hours over a water bath. (At the end of the first twenty-four hours an extremely small amount of metallic selenium had separated). The pale yellow solution was quickly filtered and cooled. /

cooled. Pale yellow needle-like crystals were obtained (m.p. 146°C). A mixed m.p. with a sample of the yellow isomeride of ditolylethylene, prepared according to Conant and Lutz (loc. cit.) gave no depression. (m.m.p. = $145/147^{\circ}\text{C}$. Yield = 1.01 g.

Concentration of the mother liquor yielded a small amount of pale yellow crystals which were crystallized from alcohol (m.p. and m.m.p. with ditolylethylene (yellow) = $145/146^{\circ}\text{C}$). Total yield = 1.03 g. corresponding to 62%.

- (11) 4-4' dimethyldiphenacyl (0.647 g.) and SeO_2 (0.2 g.) dissolved in 95% alcohol (20 cc.) together with water (1 cc.) and a drop of HCl were refluxed for 40 hours over a water bath. The pale yellow solution was separated from the precipitated selenium metal and concentration to two-thirds of its volume gave on crystallization 0.41 g. of pale yellow needles (m.p. $145/147^{\circ}\text{C}$). Mixed m.p. with a sample of ditolylethylene prepared according to Conant and Lutz, gave no depression (mixed m.p. = $145/147^{\circ}\text{C}$). Yield = 63%.

Di(p-bromobenzoyl)Ethane and Selenium dioxide:

Di(p-bromobenzoyl)ethane (0.51 g.) and SeO_2 (0.16 g.) dissolved in alcohol (70 cc.) and water (1 cc.) were refluxed for 60 hours. Very little selenium /

selenium had separated and so a drop of HCl was added and the mixture refluxed for another 20 hours. The yellow alcoholic solution was at once filtered, and on cooling deposited some pale yellow crystals. Concentration of the mother liquor yielded some more pale yellow crystals. (Yield = 0.32 g.) (m.p. and mixed m.p. with the yellow isomer of di(p-bromobenzoyl)ethylene = 184/187°C). Total yield = 64%.

Di(p-chlorobenzoyl)ethane and selenium dioxide:

Di-(p-chlorobenzoyl)ethane (0.38 g.) and SeO_2 (0.17 g.) dissolved in alcohol (15 cc.) and water (1 cc.) were refluxed for 60 hours. The pale yellow solution was, as usual, separated from the precipitated selenium and after concentration to two-thirds its volume and subsequent crystallization 0.22 g. of pale yellow needles were obtained and recrystallized from alcohol. (m.p. 170/172°C). A mixed m.p. with the yellow modification of di(p-chlorobenzoyl)ethylene, prepared according to Conant and Lutz gave no depression (m.m.p. 171/172°C). Yield = 58%

In a second experiment 4-4' dichlorodiphenacyl (0.42 g.) and SeO_2 (0.22 g.) dissolved in alcohol (20 cc.) and water (1 cc.) were refluxed for 36 hours with a drop of HCl. The pale yellow solution was, as usual, filtered and a little alcohol evaporated when 0.21 g. of pale yellow crystals were obtained which were recrystallized from alcohol (m.p. = $171/172^\circ\text{C}$). Mixed m.p. with yellow isomer of di(p-chlorobenzoyl)ethylene = $171/172^\circ\text{C}$.

4-4' Dimethoxydiphenacyl and Selenium dioxide:

Encouraged by the success of these results, it was next decided to prepare Di(p-methoxybenzoyl)ethylene by oxidizing 4-4' dimethoxydiphenacyl.

4-4' Dimethoxydiphenacyl (1.12 g.) and SeO_2 (0.46 g.) were dissolved in 95% alcohol (18 cc.) and water (1 cc.). The mixture was refluxed for 48 hours over a water bath, with a drop of HCl. After separating from the precipitated selenium, the faintly orange-yellow solution was concentrated to about one-third of its original /

original volume when a pale orange-yellow oily substance was obtained. The mother liquor was decanted off and the residue triturated with a little (10 cc. of 60/80° fraction) light petroleum. Since nothing solid was thus obtained and attempted crystallization from various solvents were unsuccessful, this pale orange-yellow oily substance was dissolved in benzene and put through a column of alumina (14" x $\frac{1}{2}$ "). A faintly yellowish orange band spread down the column and it was completely washed through as developing with the same solvent was followed. From the developed solution after evaporating off all benzene, an orange-yellow oily product was obtained, (which did not solidify even after keeping for four months).

In a second experiment where no HCl was used and the mixture, (consisting of 4-4'-dimethoxydiphenacyl (0.47 g.), SeO_2 (0.2 g.) and alcohol (20 cc.) with water (1 cc.)) refluxed over a water bath for 60 hours, the same type of (faintly orange-yellow) oily product was obtained, and this also could not be purified. It decolourized bromine water and did not appear to be enolic (FeCl_3). There was effervescence with thionyl chloride and PCl_5 , the mixture becoming deep red in colour.

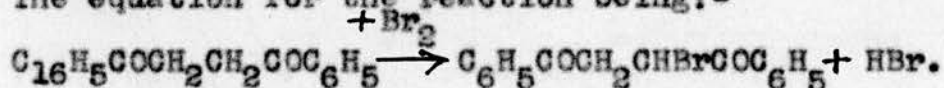
Preparation of γ -bromodiphenacyl:

I. Diphenacyl and bromine:

Diphenacyl (0.45 g.) dissolved in glacial acetic acid (10 cc.) was treated with bromine (0.1 cc.). The mixture was warmed when the solution turned straw yellow with the liberation of HBr. On cooling colourless crystals (m.p. 136/137°C) were obtained which were recrystallized from a mixture of alcohol and glacial ^{acetic} acid (1:1 ratio), when colourless plates (m.p. 138/139°C) were obtained. Yield = 0.58 g. of pure product, almost quantitative.

Analysis	Found	-----	Calculated for
			$C_{16}H_{13}O_2Br$.
Bromine	25.35%		25.2%

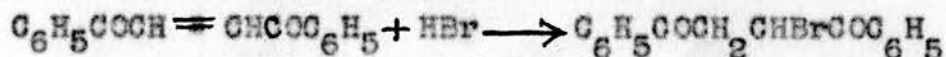
The equation for the reaction being:-



II. (Yellow) Dibenzoyl Ethylene and HBr:

(Beilstein, 7, 774).

This reaction is supposed to proceed as:-



Dibenzoyl ethylene (0.5 g. of the yellow isomer) was dissolved in warm glacial acetic acid (15 c.c. at a temp of 45/50°C). HBr was then /

then passed into this solution when in about fifteen to twenty minutes a white crystalline precipitate was obtained; the solution being colourless towards the end of the reaction. Cooled and filtered. Recrystallization of this white substance from a mixture of alcohol and glacial acetic acid (1:1 ratio) gave colourless plates (m.p. 137/138°C). Yield = 0.62 g. m.p. quoted in literature = 139°C.

A mixed m.p. of the products obtained by both these methods (I and II) gave no depression (m.m.p. = 137/138°C).

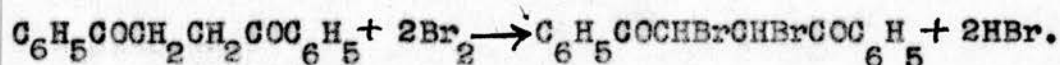
Diphenacyl and Bromine:

Prep. of α - β - dibrom- α - β dibenzoyl ethane.

Diphenacyl (1.27 g. equivalent to 1 mol.) was dissolved in glacial acetic acid (10 cc.) and bromine (0.56 cc. equivalent to 2 mols.) added. The mixture was warmed when HBr was liberated and the solution turned faintly yellow. On cooling, colourless crystals were obtained which were recrystallized from a mixture of alcohol and glacial acetic acid (1:1) 2.03 g. of colourless prisms m.p. 177/178°C.

The /

The reaction may be represented as:



trans-Dibenzoyl ethylene and bromine:

trans-Dibenzoyl ethylene (0.54 g.) dissolved in warm glacial acetic acid (10 cc. at 40°-45°C) was treated with bromine (0.12 cc.). The pale yellow solution turned colourless and on cooling, colourless crystals were obtained. Filtered and recrystallized from a mixture of glacial acetic acid and alcohol (1:1) when colourless prisms (m.p. 177°C) were obtained. Yield = 0.81 g. (m.p. quoted in literature = 178°C)

A mixed m.p. of this α - β -dibrom- α - β -dibenzoyl ethane with that obtained from diphenacyl (1 mol) and bromine (2 mols) gave no depression (m.m.p. 176/177°C).

γ -Bromdiphenacyl and quinoline /

-105-

γ -Bromdiphenacyl and quinoline

Preparation of trans-dibenzoylethylene:

γ -Bromdiphenacyl (0.65 g.) and quinoline (2 cc.) were heated together for twenty minutes at a temperature of 170-175°C.

The resulting brownish yellow reaction mixture, after cooling, was poured into dilute HCl (25 cc.) and the yellow precipitate extracted with ether, washed well with water, dried over anhydrous sodium sulphate and the ether evaporated. The yellow residue was crystallized from alcohol when 0.46 g. of pale yellow needles (m.p. 108/110°C) were obtained. Mixed m.p. with an authentic sample of trans-dibenzoylethylene gave no depression (m.m.p. = 109/110°C). Yield about 95%.

In a previous experiment where another sample of the same mixture was heated at 150/160°C for fifteen minutes 0.26 g. of the yellow isomer of dibenzoylethylene (m.p. 108/110°C) were obtained from 0.49 g. of γ -bromdiphenacyl and quinoline (1.5 cc.). Yield = 71%

Preparation of Ditoluylethylene:

Following the same procedure as above, γ -brom-dimethyldiphenacyl (0.5 g.) obtained from 4-4' dimethyl diphenacyl (0.4 g.) and bromine (0.08 cc.) in 10 cc. of glacial acetic acid) and quinoline (2 cc.) /

(2 cc.) were heated at 175/180°C for twenty minutes. The product was cooled and poured into dilute HCl (25 cc.). Extracted with ether and the dried ethereal solution on evaporation gave a pale yellow substance which was crystallized from alcohol when 0.36 g. of pale yellow needles (m.p. 145/147°C) were obtained.

Mixed m.p. with a sample of trans-di(p-)toluyl-ethylene prepared according to Conant and Lutz, gave no depression (m.m.p. - 145/147°C). Yield = 94%

Acetonylacetone and Bromine:

Acetonylacetone (1.90 g.) - 1 mol) in glacial acetic acid (7 cc.) was treated with bromine (0.88 cc. - 1 mol.). The reaction mixture was slightly warmed (30 - 35°C), when with the liberation of HBr. the whole solution turned black. This could not be worked up further.

In a second experiment acetonylacetone (1.33 g.) in glacial acetic acid (15 cc.) was likewise treated with bromine (0.62 cc.). The reaction mixture was left at room temperature for half an hour and then slightly warmed as before. It was noticed that bromine first went into the solution (solution) /

(solution almost colourless) but instantaneously it turned black as in the previous case. All attempts to stop the reaction, when the solution was pale yellow, and thus avoiding its turning black, were unavailing.

Preparation of Benzoylacetone

(Claisen, Ber. 1905, 38, 695):

Acetophenone (24 g.) and ethyl acetate (20 g.) were dissolved in dry ether (150 cc.) and the mixture, kept cool in an ice-salt bath, was treated (gradually) with sodamide (16 g.). After half-an hour the whole set to a thick paste and after a day's standing the salt was dissolved by adding it to ice-water and the aq. layer separated. Any excess of ether was removed by bubbling air through it and benzoylacetone precipitated with acetic acid (24.6 g. of a crystalline product - m.p. 60/61°C. Yield about 75%).
M.P. quoted in literature = 61°C.

Benzoylacetone and phenacylbromide

(Bedforss, Ber., 1918, 51, 198-199):

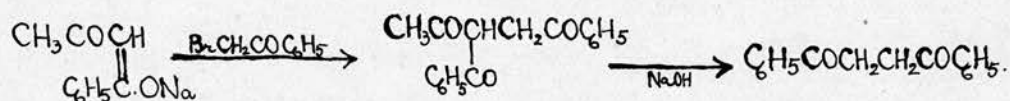
Phenacylbromide (5 g.) and Benzoylacetone (4.1 g.) dissolved in alcohol were treated with 0.57 g./

0.57 g. of sodium. The reaction mixture, which was strongly alkaline was left at room temperature for two days when a good yield of a mixture of cubical and needle-shaped crystals was obtained. These were filtered off, (most of these were cubic shaped and melted at 87/88°C. Yield = 4.32 g.)

Hydrolysis of Acetyldiphenacyl:

Acetyldiphenacyl (2.5 g.) dissolved in the minimum amount of alcohol was treated with NaOH (0.4 g. as a 5% solution) and the mixture heated for ten minutes (to about 80°C), then cooled and filtered. The colourless crystalline precipitate was dried and crystallized from alcohol (2 g. of colourless needles, m.p. 142/143°C and mixed m.p. with an authentic sample of diphenacyl = 142/144°C). Yield = 93%.

The reactions may be represented as:



Working on the same lines, attempts were made to prepare (o-mononitro)-Dibenzoyl ethane, (m-mononitro)dibenzoyl ethane and (p-mononitro)-dibenzoyl ethane.

Benzoylacetone and ω-monobromo-o-nitroacetophenone:

(1) /

(1) ω -monobromo-o-nitroacetophenone (5.5 g.) and benzoylacetone (3.65 g.) dissolved in alcohol (25 cc.) were cooled in an ice-salt bath and sodium (0.510 g.) added. In a few minutes (five to ten) a precipitate was obtained. It was filtered but attempts to crystallize it were unsuccessful.

(11) The experiment was repeated and this time the mixture was kept, as in the case of Acetyldiphenacyl, for two days at room temperature. Filtered and crystallization of the faintly yellowish precipitate attempted but with no success.

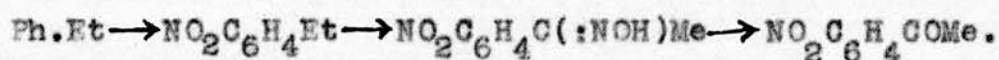
Hydrolysis of the precipitate (obtained in the above two experiments) with NaOH gave a brown oily substances which in their turn were difficult to purify.

The same difficulties were encountered in the reactions between benzoylacetone and ω -monobromo-meta, (and para)-nitroacetophenone.

In view of these difficulties, the reaction between o-nitrobenzoylacetone and ω -monobromo-o-nitroacetophenone was not carried out.

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Ortho-and Para-nitroacetophenones were prepared according to Rydon and Ford-Moor(J.C.S.,1946,679) by the nitration of ethyl benzene followed by preparation of o-and p-nitroacetophenone oximes from o-and p-nitro-ethyl benzenes, sodium tert.-butoxide and tert.butyl nitrite, and subsequent hydrolysis of the oximes with dil. H_2SO_4 .



For a quick preparation of m-nitroacetophenone the method of Elson and Gibson (J.C.S.1930,1131) was used.

Acetophenone in lots of 30 cc. was run slowly into stirred HNO_3 (d.1.5),140cc. being used each time, and the temperature kept below $0^\circ C$. After half an hour the product was poured on crushed ice and crystalline m-nitroacetophenone separated and recrystallized from alcohol.

Preparation of ω -monobromo-o-nitroacetophenone
(Gevekoht-Annalen,221,327-333):

O-nitroacetophenone (1 mol.) dissolved in three times its amount of glacial acetic acid was treated with bromine (1 mol.) and the mixture slightly warmed. HBr was liberated and the solution turned straw yellow; It was cooled and treated with crushed ice when a pale yellow oily substance separated at the bottom. Its crystallization from ligroin gave colourless needles (m.p. $55^\circ C$).

Preparation of ω -monobrom-m-nitroacetophenone
(Evans and Brock,J.A.C.S.30,404 (1908)).

12.1 g. of bromine in 20cc of chloroform solution were allowed to flow slowly into a warm solution of 12.48 g. of m-nitroacetophenone in 80cc. of the same solvent, the operation being carried out in sunlight. From the pale yellow solution /

solution, after the evolution of HBr had ceased, chloroform was removed and the residue taken up in ether. After being washed with dilute Na_2CO_3 solution and water, the ethereal solution gave 17.8 g. of a pale yellow crystalline substance (m.p. 95/96°C). Yield = about 96%

m-Nitrobenzoylformaldehyde was prepared according to Evans and Witzemann, (J.A.C.S.33,1773): 7 g. of ω -monobromo-m-nitroacetophenone suspended in 350 cc. of water were treated with 4.82 g. of silver nitrate and the mixture refluxed for two hours. AgBr was then filtered off and the filtrate immediately treated with one gram of CaCO_3 . Extraction with ether, washing with water, drying and subsequent distillation of ether gave 3.8 g. of m-nitrobenzoylformaldehyde as a straw yellow viscous oil.

m-Nitrobenzoylformaldehyde and m-Nitroacetophenone:

1.85 g. of m-nitrobenzoylformaldehyde with 1.65 g. of m-nitroacetophenone in 15 cc. of glacial acetic acid and a drop of concentrated sulphuric acid were refluxed for an hour and a half. After cooling it was poured into 100 cc. of cold water and after extraction with ether, washing with dilute sodium carbonate solution and water, the yellow ethereal solution was dried over CaCl_2 and the ether evaporated. The orange oily /

12

oily substance thus obtained was boiled with 50 cc. of light petroleum (60/80°) whereby most of the unreacted m-nitroacetophenone was removed. The residual orange coloured oily product was dissolved in chloroform and put through a column of alumina (15" x $\frac{3}{4}$ "), as attempts to crystallize by various solvents failed. A pinkish orange band spread down the column ($1\frac{1}{2}$ " long) and as developing with chloroform was continued a very pale yellow band ($\frac{1}{2}$ " long) moved down the column, while the pinkish band remained almost stationary. Developing of the yellow band and subsequent concentration of the yellow developed solution gave 0.21 g. of pale yellow crystals (m.p. 77/78°C). A mixed melting point with m-nitroacetophenone showed no depression (m.m.p. = 78°C). From the top (pinkish) band, all attempts to isolate anything (e.g. washing with alcohol, extraction by hot alcohol using a soxhlet apparatus, etc.) proved unsatisfactory.

m-Nitroacetophenone and Phenylglyoxal:

3.6 g. of Phenylglyoxal with 3.8 g. of m-nitroacetophenone in 12 cc. of glacial acetic acid and a drop of concentrated sulphuric acid were refluxed for two hours: Cooled and poured the deep yellowish-brown reaction mixture into 150 cc. of cold water. After extraction /

extraction with chloroform, washing it with dilute Na_2CO_3 solution, it was dried over anhydrous Na_2SO_4 and chloroform evaporated, when an orange-yellow resinous mass was obtained. It was soluble in alcohol but sparingly so in light petroleum. Attempts to purify it by various solvents did not give much help. It was therefore dissolved in benzene and put through a column of de-activated alumina ($20'' \times \frac{3}{4}''$). A pinkish orange band spread down the column and further development with the same solvent was continued when a faintly yellow band began to separate and although moving slowly, it was washed through and after concentration of the pale yellow developed solution, pale yellow needles (m.p. $78/89^\circ\text{C}$) were obtained. These were identified (by a mixed melting point) as m-nitroacetophenone.

From the top pinkish band, developing with alcohol and extraction with boiling alcohol and boiling chloroform gave unsuccessful results.

In another experiment when lactose was substituted for de-activated alumina, the whole of the substance (that was to be purified) moved down very quickly as one band, giving no separation.

Attempts to prepare (o-mononitro)di-benzoyl-ethylene from o-nitroacetophenone and phenylglyoxal met with the same difficulties.

p-N-Acetylaminoacetophenone:

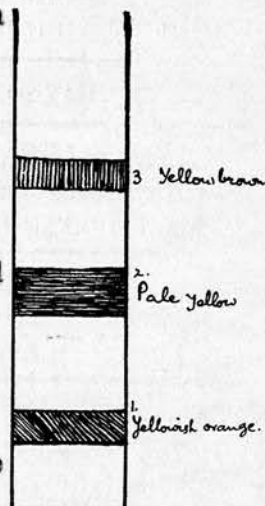
p-aminoacetophenone (5 g.) was treated with acetic anhydride (10 cc.) and a drop of concentrated H_2SO_4 . After heating for five minutes it was cooled and water added drop by drop till precipitation occurred. The white precipitate thus obtained was crystallized from alcohol (melting point 166°C . Yield, almost quantitative).

Condensation with Phenylglyoxal:

p-N-acetylaminoacetophenone (2.23 g.) and phenylglyoxal (1.53 g.) in 10 cc. of glacial acetic acid and a trace of concentrated H_2SO_4 (one drop of the latter in 60 cc. of glacial acetic acid) were refluxed for two and a half hours. The mixture was cooled and poured into 100 cc. of cold water and extracted with chloroform. The chloroform layer was washed well with water, dried over anhydrous sodium sulphate, and the chloroform evaporated. The residual yellowish-brown substance was chromatographed on a column of alumina ($14" \times \frac{1}{2}"$) with chloroform as solvent. As developing was continued, three different bands separated down the column.

1. A yellowish /

1. A yellowish orange band. Evaporation of chloroform gave an orange-yellow resinous product (0.7 g.) All attempts to crystallize it were unsuccessful. It was next dissolved in CHCl_3 and put through a short column of lactose, but this did not help as no purification was possible since the whole of the substance moved down as an orange yellow band swiftly.



2. A pale yellow band which was developed as usual. Evaporation of chloroform gave a pale yellow solid m.p. $160/161^\circ\text{C}$. Recrystallization from hot water gave very faintly yellow (almost colourless) crystals, m.p. $164/165^\circ\text{C}$. Mixed m.p. with p-N-acetyl amino acetophenone gave no depression. Yield = 1.41 g.
3. After the pale yellow band had been washed through, the top yellowish-brown band (which did not move down), was cut from the rest of the column and extracted with hot chloroform using a soxhlet. The brown coloured substance (0.33 g.) obtained after evaporation of chloroform was difficult to crystallize and so it was again dissolved in chloroform and put through a column of lactose ($9'' \times \frac{1}{2}''$). A yellow brown band ($2''$ long) spread down this column and was washed through completely as developing with chloroform was continued.
- Chloroform /

Chloroform was evaporated and since all attempts to crystallize this substance were unsuccessful, it was not investigated further.

Phenylglyoxal and p-Nitroacetophenone:

p-Nitroacetophenone = 3.80 g.

Phenylglyoxal = 3.55 g.

Glacial acetic acid = 13 cc.

p-Nitroacetophenone (3.8 g.), phenylglyoxal (3.55g.) and glacial acetic acid (13 cc.) containing a trace of concentrated H_2SO_4 (one drop in fifty cc.) were refluxed for two hours. The deep brown reaction mixture, after being cooled, was poured into 200 cc. of cold water. It was extracted with chloroform, washed well with water and dried over anhydrous Na_2SO_4 . The chloroform was evaporated and the yellowish brown resinous product treated with 50 cc. of ether. The pale yellow ethereal solution was decanted off and the residue crystallized from alcohol, when a pale yellow crystalline product (m.p. 145°C uncorr.) was obtained (A). From the ethereal solution after evaporation, a yellow substance was obtained. It was crystallized from light petroleum, when a pale yellow crystalline substance m.p. $76/78^\circ\text{C}$. was obtained. Its mixed m.p. with p-nitroacetophenone gave no depression (m.m.p. = $76/79^\circ\text{C}$).

The substance (A) above was recrystallized from /

from benzene when yellow plates (m.p. 145/146°C) were obtained.

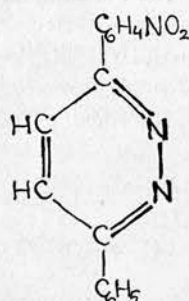
Analysis	Found	Theoretical for $C_{16}H_{11}O_4N$
Carbon	67.2%	68.3%
Hydrogen	4.28%	3.91%
Nitrogen	5.01%	4.98%

Analysis was satisfactory.

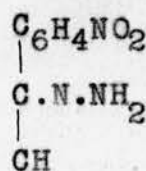
Another sample, after further crystallization from benzene, gave on analysis: C = 67.43% and H = 4.98%

Reaction with hydrazine hydrate: 0.1 g. of this yellow substance (m.p. 145/146°C). was dissolved in 8 cc. of glacial acetic acid and hydrazine hydrate (1 cc. of 50% solution) added. The solution was heated almost to boiling and then cooled. A very pale yellow precipitate was thus obtained which was recrystallized from alcohol - glacial acetic acid mixture (in 1:1 ratio). A very pale yellow (almost colourless) crystalline substance was obtained (m.p. 234°C corr.)

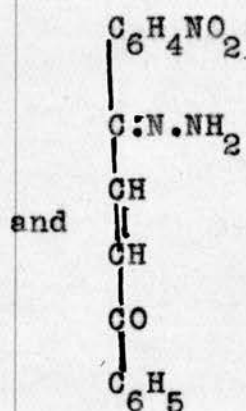
Analysis gave nitrogen = 12.8% whereas the theoretical value for



i.e. $C_{16}H_{11}O_2N_3$, Nitrogen = 15.16%



/ See next page



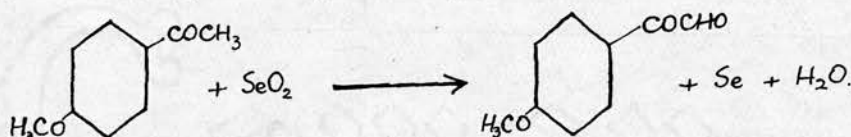
i.e. $\text{C}_{16}\text{H}_{13}\text{O}_3\text{N}_3$, the value of nitrogen = 14.2%

*Analysis
unsatisfactory.*

$\text{C}_{18}\text{H}_{15}\text{O}_4\text{N}_3$
 $\text{C}_{16}\text{H}_{13}\text{O}_3\text{N}_3 + \text{CH}_3\text{CO}$
 requires N, 12.5%

Attempted preparation of p-methoxybenzoylformaldehyde:

Assuming the reaction to proceed as in the case of Phenylglyoxal, namely:



it was decided to prepare p-methoxybenzoylformaldehyde from p-methoxyacetophenone.

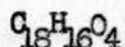
p-Methoxyacetophenone (20 g.) was added in one lot to a solution of SeO_2 (15 g.) dissolved in 95% alcohol (100 cc.) and water (7 cc.). The mixture was heated over a water bath at 50-58°C for five and a half hours with continuous shaking. The yellow solution was separated from the precipitated selenium and most of the alcohol and water removed by distillation. The residual yellow liquid was distilled under reduced pressure. At 150/158°C and 20 mms., a very small amount (2.3 g.) of a yellow viscous oil distilled over while the residue in the flask became almost black and nothing further could be isolated.

1. Attempted preparation of Di(p-methoxybenzoyl) ethylene:

p-Methoxybenzoylformaldehyde (1.8 g.) and p-methoxyacetophenone (1.7 g.) in 50 cc. of acetic anhydride were refluxed together for three hours. The mixture was cooled, poured in water and extracted with ether. The dried ethereal solution on evaporation of ether gave a yellowish oily residue which was then steam distilled and crystallized from alcohol. Pale yellow (prisms) m.p. 117°C . were obtained.

An alcoholic solution of it was exposed to sunlight for six hours and evaporation of alcohol and subsequent recrystallization gave an almost colourless substance, m.p. $123/125^{\circ}\text{C}$. Mixed m.p. with the product before gave no depression. Apparently no conversion took place - only the substance was obtained in a purer state.

Analysis: Found - Calculated for



Carbon	70.12%	73%
Hydrogen	5.46%	5.405%

*Unsatisfactory
analysis.*

2. In another experiment where glacial acetic acid and a drop of concentrated H_2SO_4 was used instead of glacial acetic acid, a brownish orange tarry product was obtained which was difficult to crystallize.

p-N-acetylamino-acetophenone and SeO₂:

An attempted preparation of p-N-acetylamino benzoyl-formaldehyde from p-N-acetylaminoacetophenone (15 g.) and SeO₂ (10 g.) dissolved in 95% alcohol (100 cc.) and water (10 cc.) was not successful. Although five and a half hours' heating at 55-60°C resulted in the precipitation of metallic selenium, and the solution was orange yellow, yet after removing excess of alcohol and water, the residual (greenish)-orange liquid could not be distilled under the available reduced pressure (14 mms.). The substance in the flask decomposed as the distillation was carried out.

Attempted preparation of p-Nitrobenzoyl acetic ester:

(Cf. Dorsch and McElvain, J.A.C.S. 1932, 54, 2963)

In a preliminary experiment, benzoyl acetic ester was prepared by heating ethyl benzoate (17 g.), ethyl acetate (10 g.) and sodium ethoxide (7.72 g.) at 80°C for three hours. (Ethyl acetate was gradually added to the other two reactants over a period of an hour). After decomposing with dilute acetic acid and fractionally distilling under reduced pressure, 4.9 g. of the ester were collected at 153/162°C at 14 mms. Yield about 22%.

In spite of the yield being low, an identical procedure /

procedure was employed to bring about a direct condensation between methyl-p-nitrobenzoate and ethyl acetate in presence of NaOMe. This experiment resulted in the formation of a yellowish brown substance (m.p. 170/174°C). As it did not appear to be the expected ester, it was not investigated further.

Preparation of Chloroacetyl chloride:

(Barnett - Chem. News 1921, 122, 220).

Monochloroacetic acid (32 g.) and thionyl chloride (44 g.) were heated gently on a water bath. After the initial reaction was over, the mixture was heated over a wire gauze and when the evolution of gases ceased, the resultant colourless liquid was distilled and the fraction coming over at 100-110°C collected. Redistillation gave 29.8 g. of chloroacetyl chloride. Yield = 78%.

Preparation of ω -chloro-p-methoxyacetophenone:

(Tutin, J.C.S., 97, 2503).

Anisole (28 g.) mixed with chloroacetyl chloride (30 g.) and carbondisulphide (150 cc.) was kept cool in an ice bath and under continuous stirring by means of a mechanical stirrer was treated gradually with dry powdered aluminium chloride. After three hours, ~~the~~ CS₂ was decanted off, the residue /

residue decomposed by ice and HCl and the product extracted with ether. The ethereal layer was washed with aq. NaOH solution and water, and ether then evaporated. Fractional crystallization of the residue with alcohol gave ω -chloro-p-methoxyacetophenone (m.p. 100/101°C) while ω -chloro-o-methoxy acetophenone remained in solution.

Attempted preparation of sym-Di(p-methoxybenzoyl)-ethylene:

(Cf. Bogoslovskii, J.Gen.Chem.(U.S.S.R.), 14, 993-4; C.A.1945, 39, 4600)

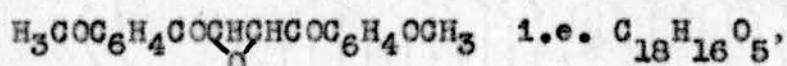
ω - chloro-p-methoxyacetophenone (7.1 g.) dissolved in 25 cc. of alcohol was treated with KOH (2.2 g.) dissolved in alcohol (10 cc.) and water (2 cc.). The solution immediately turned deep orange in colour and some precipitate separated out. After shaking for five minutes, the mixture was treated with 200 cc. of cold water, when an orange-brown substance separated out. This was at once extracted with ether, (as filtration was unsatisfactory) and the ethereal layer washed well with water and the ether evaporated. The yellow resinous product thus obtained was next boiled with 100 cc. of light petroleum (100/120°C) and separated from the orange-brown tarry product which in its turn could not be purified.

The /

The ligroine solution, after evaporation to dryness yielded a yellow oily substance which was then triturated with methylalcohol and the colourless solid thus obtained was recrystallized from the same solvent when colourless plates (m.p. 148°C) were obtained. Yield = 1 g. app.

Analysis	Found	Theoretical for $C_{18}H_{16}O_4$
Carbon	69.98%	73%
Hydrogen	4.7%	5.4%

whereas for,



Th. C = 69.23% and H = 5.1%

Preparation of sym-Di(o-nitrobenzoyl)ethylene:

ω -Monobromo-o-nitroacetophenone (5.1 g.) dissolved in warm alcohol (40 cc. at 35-40°C) was treated with KOH solution (1.19 g. dissolved in 10 cc. of alcohol and 2 cc. of water). The reaction mixture immediately turned reddish brown and after good shaking for five minutes was treated with cold water (200 cc.) and filtered at once under suction. The orange-yellow precipitate thus obtained was sucked as dry as possible and next taken up in about 15 cc. of glacial acetic acid. It was filtered and the filtrate diluted with about 20 cc. of water and the yellowish precipitate /

precipitate thus obtained recrystallized from alcohol and glacial acetic acid mixture (1:1 ratio). About 0.5 g. of colourless needles were obtained. (m.p. 163/164°C). It was not investigated further since reaction with hydrazine hydrate was not satisfactory. Analysis: $\begin{array}{l} \text{Found} \\ \text{Th.} \end{array} \begin{array}{l} \text{C} = 58.46\% \\ \text{H} = 3.10\% \end{array} \begin{array}{l} 58.9\% \\ 3.06\% \end{array} \text{C}_{10}\text{H}_{10}\text{O}_2\text{N}_2$

A sample of it after treatment with hydrazine hydrate solution in cold glacial acetic acid yielded nothing. The mixture was next heated for about five minutes (almost to boiling), cooled and a few drops of water added. A gelatinous precipitate was thus obtained which however could not be purified as all attempts to crystallize it out by various solvents were unsuccessful.

In a second experiment of this series, ω -monobromo-m-nitroacetophenone (5 g.) was likewise dissolved in warm alcohol (40 cc. at 35/40°C) and treated with a solution of KOH (1.2 g.) in alcohol (10 cc.) and water (2 cc.). The reddish brown reaction mixture, after five minutes' shaking, was treated with cold water (200 cc.) and though the solution had a pink turbidity about a gram of a yellowish substance was left behind on the filter. It was sucked as dry as possible.

Attempts to extract some more material from the filtrate by means of ether yielded an orange oily product which was difficult to be crystallized.

The /

The residue on the filter was next taken up in glacial acetic acid and thrown down by the addition of some water, as in the case of the ortho-isomeride above.

Although the colour of the precipitate was much paler than before (pale yellowish), yet its crystallization from various solvents could not be accomplished.

Similar difficulties were experienced when preparation of sym-Di(p-nitrobenzoyl)ethylene from ω -mono-bromo-p-nitroacetophenone was attempted.

In several ^{preliminary} experiments during the preparation of dibenzoyl ethylene, di-p-bromobenzoyl ethylene etc., it was found that any delay in the filtration of the precipitate (after treating the reaction mixture with cold water), invariably resulted in the formation of resinous products whose purification was thereby further complicated.

In the case of di(p-bromobenzoyl)ethylene, only a very minute amount of it could be obtained (crystallized from light petroleum). The rest of the material appeared to be of a different kind since it gave no satisfactory result with hydrazine hydrate.

Preparation /

Preparation of Dimethylfumarate:

(Purdie, J.C.S. 1881, 39, 346).

Fumaric acid (20 g.) dissolved in methyl alcohol (125 cc.) was treated with concentrated sulphuric acid, (5 g.) and the mixture refluxed over a water bath for six hours. About 45 cc. of methyl alcohol was distilled off and the residue in the flask on cooling deposited colourless crystals which were filtered, washed with a little methyl alcohol and dried. 21.8 g. of dimethylfumarate (m.p. 100/101°C) were obtained as colourless leaflets. (Yield = 85% of the theoretical.)

Preparation of Fumardiamide: (McMaster and Langreck, J.A.C.S. 1918, 40, 970).

Dimethylfumarate (20 g.) together with NH_4OH (90 cc., sp. gravity = 0.88), allowed to stand for twenty-four hours at room temperature with occasional stirring. Fumardiamide formed as a fine white powder which was filtered and dried. Yield = 14 g. (m.p. above 260°C - as it began to decompose at this temperature).

88% of the theoretical.

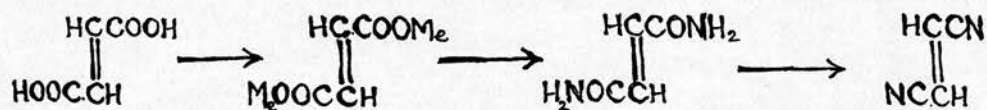
Preparation of Fumaric nitrile: Fumardiamide (14 g.) was mixed with phosphorous pentaoxide (35 g.) and with careful heating distillation under reduced pressure carried out when colourless needle /

needle-like crystals (m.p. 94/96°C) were obtained.

Yield → 8.05 g.

corresponding to about 83% of the theoretical.

The reactions may be written as:



Phenylmagnesiumbromide was prepared from magnesium metal flakes, freshly distilled bromobenzene and dry ether in the usual way. Sometimes it was necessary to start the reaction by rubbing with the help of a glass rod, one or two magnesium metal flakes, against the sides of the reaction vessel. The mixture first became turbid and towards the end of the reaction it was brown in colour. Most of the unreacted magnesium, except a few remnants (about 0.02 mg. or so) was sent into solution by gently warming the solution over a water bath, and the resulting brownish coloured reaction mixture was then ready for further work.

Fumaric nitrile and Phenylmagnesiumbromide:

Fumarionitrile (1.24 g.) dissolved in dry ether (25 cc.) was treated with phenylmagnesium bromide (5.6 g.). After shaking for five minutes and gently warming for two minutes (to 30/35°C), the reaction mixture was decomposed with 35 cc. of 10% H₂SO₄ and 25 g. crushed ice. The orange-brown ethereal solution was separated, dried over anhydrous Na₂SO₄ and the ether evaporated. An intensely /

intensely deep brown, (almost black) substance was obtained and attempts to purify it were unavailing.

Phenylmagnesiumbromide and Succinonitrile:

Succinonitrile (1.604 g.) dissolved in dry ether (50 cc.) and dry benzene (10 cc.) was treated with phenylmagnesiumbromide (7.3 g.). An instantaneous white precipitate, which in a few seconds changed to pale yellow, was obtained. After five minutes' shaking of the mixture, it was treated with 10% H_2SO_4 (50 cc.) and crushed ice (30 g.) when a large amount of greenish brown resinous product separated out, and this could not be purified although its alcoholic solution on leaving overnight turned deep greenish-brown. From the ether-benzene layer - after separation from the aq. layer and subsequent evaporation of ether and benzene a greyish white residue was obtained. Crystallization from methanol gave colourless crystals (m.p. 78/81°C micro and 67°C on ordinary apparatus). Recrystallization from methanol again, gave colourless crystals (m.p. 67/68°C on ordinary apparatus (corr.) while 80/81°C on micro).

Analysis gave : C = 92.8% and H = 6.66%

For diphenyl the theoretical values are:

C = 93.5% and H = 6.49%

A mixed m.p. with diphenyl, was therefore necessary, and there was no depression (m.m.p. = 68/69°C ordinary).

When instead of 10% H_2SO_4 the initial reaction mixture was decomposed by ice cold solution of NH_4Cl and dilute HCl , no successful results were obtained. As in previous case, a very dark brownish resinous product was obtained.

The same results were obtained, using the same decomposing agents when eight mols. of phenylmagnesium bromide were used (cf. Shriner and Turner, J.A.C.S., 52, 1268), Diphenyl (identified by m.p. and m.m.p.) being obtained along with the resinous products.

Preparation of p-nitrobenzoyl chloride:
(Frankland and Harger, J.C.S., 85, 1576.)

p-Nitrobenzoic acid (50 g.) and PCl_5 (64 g.) were mixed together and the mixture heated for half an hour over a water-bath. Distillation under reduced pressure yielded (at $148/154^\circ\text{C}$ at 15 mms.) 50.2 g. of a pale yellow substance. (m.p. $73/74^\circ\text{C}$).

Preparation of ethyl p-nitrobenzoylacetoacetate:

Sodium (6.2 g.) was dissolved in alcohol (100 cc.) and the solution divided into two equal parts. One of these was added to ethylacetoacetate (18.0 g.) placed in a three necked flask, fitted with a mechanical stirrer and a dropping funnel and surrounded by an ice-salt bath.

p-Nitrobenzoyl chloride (12 g.) was gradually added, the mixture being kept stirred and care being /

being taken that the temperature of the reaction mixture did not rise above 5°C . After half an hour, one half of the remaining sodium ethoxide solution was added and five minutes later another six grams of p-nitrobenzoyl chloride were added under the same conditions as before. Stirring was continued for another half an hour and the remaining NaOEt solution and p-nitrobenzoyl chloride added as previously. After stirring for another two hours, the mixture was left overnight at room temperature and the thick yellow precipitate that had settled below, filtered over suction and dried.

Preparation of Ethyl-p-nitrobenzoylacetate:

The crude sodium compound of ethyl-p-nitrobenzoylacetate (25 g.) prepared above, was mixed with a solution of NH_4Cl (6 g.) in water (120 cc.) and treated with a (conc) solution of ammonia (5 cc.) diluted with water (20 cc.). The mixture was vigorously shaken and as soon as the sodium compound had gone into solution (a little, five to ten minutes' gentle heating at 30°C ,/the whole was mixed with crushed ice (300 g.) acidified with HCl and extracted at once with ether. The dried ethereal solution on evaporation gave 5.1 g. of crude ethyl p-nitrobenzoylacetate as an orange oil. (A small amount (0.25 g.)) was let stand overnight in vacuum over concentrated H_2SO_4 when a pale yellow solid together with a little orange oil /

oil was obtained. It was triturated with methanol when a pale yellow crystalline product m.p. 68/72°C was obtained). M.P. of ethyl-p-nitrobenzoylacetate quoted in literature = 74/76°C.

The sodium salt was obtained by treating ethyl p-nitrobenzoylacetate (3.8 g.) with NaOEt (1.09 g.) and dry ether (50 cc.). It was obtained as an orange-yellow precipitate.

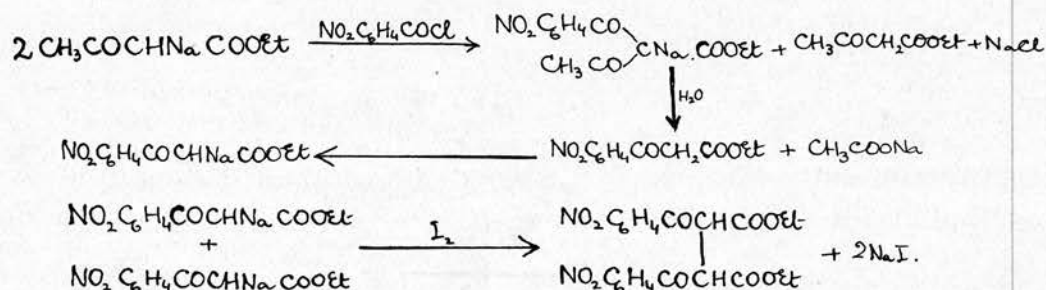
Preparation of Diethyl di-paranitrobenzoylsuccinate:

(Perkin and Bellenot, J.C.S. 1886, 49, 452)

The sodium salt of ethylic paranitrobenzoyl-acetate suspended in ether solution (obtained above), was treated with iodine (2.08 g.), dissolved in dry ether (50 cc.) under vigorous stirring. The colour of iodine quickly disappeared in the initial stages, but very slowly towards the end of the addition of this iodine solution. After two and a half hours' stirring, the mixture was treated with water (100 cc. - ice cold) and excess of iodine removed by adding a just amount of sulphurous acid and the resulting pale yellow ethereal solution separated, washed well with water, dried over CaCl_2 and ether evaporated. An orange-yellow oily substance was thus obtained which practically solidified after standing over concentrated H_2SO_4 in vacuum overnight. Trituration with methanol gave a faintly yellowish substance m.p. 172/176°C. Recrystallization from aq. alcohol yielded a better sample /

sample as that melted at 175/178°C. (m.p. quoted in literature = 180°C)

The whole series of reactions may be represented as follows



Hydrolysis of Diethyl diparanitrobenzoylsuccinate:

With 3% NaOH (aq. solution): The ester (2.1 g.) was treated with 3% aq. NaOH solution (15 cc.) and the mixture gently warmed to about 45°C. After five minutes the clear pale yellowish-brown solution was cooled and solidified with HCl, when a pale yellow precipitate^{was} obtained. This was filtered and crystallized from hot water when faintly yellow leaflets m.p. 236/237°C were obtained.

Analysis gave: C=50.3%, H=3.0% and nitrogen=8.15%
whereas
for p-nitrobenzoic acid C=50.3%, H=3.0% and nitrogen=8.4%

A mixed m.p. of the hydrolyzed product with p-nitrobenzoic acid gave no depression as the mixture melted at 235/237°C.

Hydrolysis with 1% aq. NaOH solution also resulted in the formation of p-nitrobenzoic acid (identified by m.p. and mixed m.p. = 235/237°C).

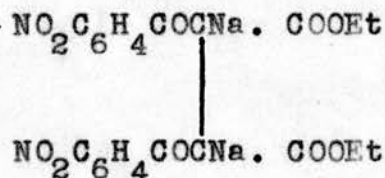
Hydrolysis with sirupy phosphoric acid:

Hydrolysis with sirupy phosphoric acid:
 Ethylidiparanitrobenzoylsuccinate (0.8 g.) with phosphoric acid (8 cc.) was heated to a temperature of 50-55°C for half an hour. It was cooled and treated with 100 cc. of water, when a pale yellow brown resinous product was obtained. Extraction with boiling water gave a very small amount (about 0.05 g.) of a pale yellow oily substance which also behaved as an acid. This, as well as the rest of the resinous product, could not be crystallized.

Employing an exactly similar procedure the corresponding meta-derivative was prepared, but at the hydrolysis stage the same difficulties were experienced. Hydrolysis with 5% and 2% aqueous NaOH solution yielded m-nitrobenzoic acid which was identified by m.p. and m.m.p. (both being 137/139°C). Analysis also showed that the hydrolyzed product was m-nitrobenzoic acid.

Analysis	Found	Theoretical for m-nitrobenzoic acid.
Carbon	50.0%	50.3%
Hydrogen	2.74%	3.0%

It was thought that preparation of _____ might be able to give some useful result:



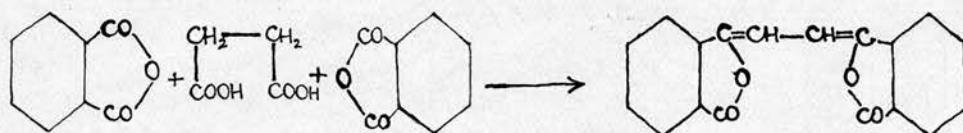
Ethylidiparanitrobenzoylsuccinate (0.58 g.) and NaOEt (0.17 g.) were mixed together in dry ether /

ether (35 cc.) and the solution after evaporation to dryness (a very faintly yellow substance being obtained) was redissolved in dry ether (50 cc.) and a solution of iodine (0.29 g.) in dry ether (45 cc.) added. The resulting brownish solution was treated with 100 cc. of water and excess of iodine removed by treatment with sulphurous acid. The ethereal layer was separated, dried and ether evaporated. The pale yellowish resinous mass (lack of material prevented its purification) was treated with 1% (10 cc.) of aq. NaOH solution, but the formation of a yellowish resinous product (yield = 0.3 g.) which could not be purified failed to give any help.

Preparation of Ethinedipthalide (Gabriel and Leupold, Ber. 31, 1159):

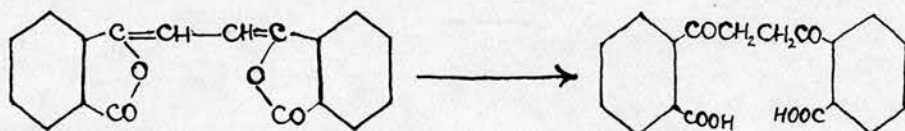
Phthalic anhydride (80 g.) and succinic acid (80 g.) were fused together in a litre-capacity round bottomed flask fitted with an air condenser and heated in an oil-bath (temp. 210°C). Dry powdered potassium acetate (22 g.) was gradually added with a slow swirling round of the reaction mixture and the whole then maintained at $210/220^{\circ}\text{C}$ for two hours. In the course of about half an hour an orange yellow crystalline product began to separate from the deep yellowish orange liquid. After cooling to about 100°C , hot water (100 cc.) was added and steam passed in it till all the lumps /

lumps disintegrated. It was filtered under suction, washed with hot water and alcohol. After drying, 50.5 g. of an orange-yellow crystalline substance (m.p. above 350°C) was obtained. Crystallization from nitrobenzene yielded δ yellow (needle-shaped) crystals (m.p. above 350°C).



Preparation of Diphenacyl di(o-)carboxylic acid:

The orange-yellow substance obtained above (30 g.) was boiled with aq. KOH (12 g. in 75 cc. of water), under reflux for two and a half hours. The deep yellow solution, with a slight violet tinge was filtered, cooled and acidified with HCl. A pale yellow oily substance was obtained which after being left in ice cold water for half an hour, solidified to a very pale yellow substance. It was filtered and dried, when 30.3 g. of the acid (m.p. $166/168^{\circ}\text{C}$) were obtained.



Preparation of Diethyl ester:

(1) Diphenacyldicarboxylic acid (5 g.) was dissolved in ethyl alcohol (25 cc.) and concentrated H_2SO_4 (1 g.) added. The mixture was /

(1) Contd.-

was refluxed for an hour; filtered and cooled. A colourless crystalline substance separated out which was removed by filtration (m.p. 202°C - yield 0.30 g.) and crystallized from a mixture of alcohol and glacial acetic acid (1:1 ratio). From the filtrate, after concentration, a brownish yellow oil was obtained, (fairly soluble in alcohol), and it was found to consist of a large amount of the unreacted acid.

Analysis of the colourless product gave
 $\text{C} = 68.82\%$ and $\text{H} = 5.70\%$

The theoretical values for the di-ester

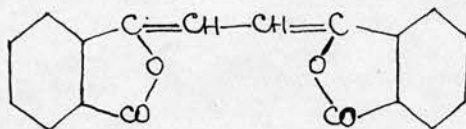
($\text{C}_{22}\text{H}_{22}\text{O}_6$) are: $\text{C} = 69.11\%$ and $\text{H} = 5.75\%$

(11) The experiment was repeated and this time the reaction mixture refluxed for three and a half hours. Along with the colourless substance there were found to be some yellow needles also which were separated by taking up the colourless substance in hot alcohol and glacial acetic acid (1:1) mixture. The yellow needles were then crystallized from nitrobenzene (0.1 g., m.p. above 350°C , showing no depression with ethine-diphthalide). Mixture did not melt below 350°C .

(111) Dry HCl gas was passed for four hours into an (ethyl)alcoholic solution of the acid, when a yellow crystalline substance separated out. Filtered over suction, washed with a little alcohol and dried. (m.p. above 350°C and no depression in m.m.p. with ethinediphthalid)

Crystallized from nitrobenzene.

Analysis gave: C = 73.96% and H = 3.58% whereas
for



$C_{18}H_{10}O_4$, the calculated values are:

C = 74.4% and H = 3.44%

Preparation of p-nitrobenzylester:

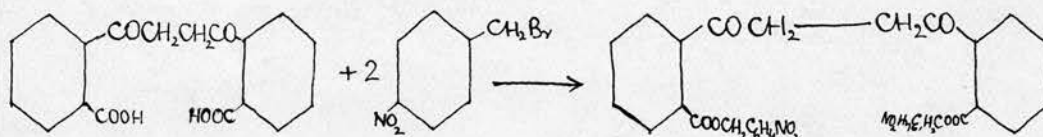
Diphenacyldicarboxylic acid (3.1 g.) was treated with water (12 cc.) and just neutralized with 10% NaOH solution. A drop of HCl was added and p-nitrobenzylbromide (4.115 g.) dissolved in alcohol (35 cc.) added. The mixture was refluxed for three hours, cooled and the crystalline precipitate thus obtained filtered, washed with a little alcohol, and crystallized from glacial acetic acid when colourless crystals (m.p. 183/184°C) were obtained.

Analysis: Found Theoretical ($C_{32}H_{24}O_{10}N_2$)

Carbon = 64.23% 64.43%

Hydrogen = 4.07% 4.02%

The equation for the reaction is:



Preparation of Benzylester:

(1) Using Benzylchloride: Diphenacyldicarboxylic acid (1.514 g.) suspended in 5 cc. of water were /

(1) Contd.-

were just neutralized with 10% NaOH solution. A drop of HCl was added and Benzylchloride (1.18 g.) with 10 cc. alcohol added. The mixture was refluxed for three hours. Cooled and left overnight, an orange-red Oil (A) separated (very soluble in alcohol). To the decanted solution 25 cc. of light petroleum (60/80°C) were added and the white precipitate thus obtained (weight 0.01 g.) was filtered and dried. (m.p. 165/167°C (Ordinary) and mixed m.p. with diphenacyl di-carboxylic acid showed no depression (m.m.p. 164/167°C). The oily substance (A) was taken up in alcohol and ether and the alcohol-ethereal solution shaken with Na_2CO_3 solution and the lower (aq) layer separated and acidified with HCl. A brownish yellow solid was precipitated (m.p. 161/165°C after purification with aq. alcohol). From the alcoholic ethereal layer after evaporation of alcohol and ether a faintly brownish resinous product was obtained. After trituration with light petroleum (B.P. 100/120°C) it was treated with dilute Na_2CO_3 solution when the whole of it dissolved. Acidifying with HCl resulted in a pale yellowish brown resinous product which was difficult to crystallize.

(11) /

(11) The experiment was repeated but this time the mixture was refluxed for 16 hours. In this case also practically the whole of the acid was obtained back.

(111) Using Benzyl iodide:

Benzyl iodide was prepared according to Späth (Monatsch, 1913, 34, 1995), from Benzyl Chloride and KI.

As before, the acid (2.781 g.) suspended in 12 cc. of water was just neutralized with 10% NaOH solution and two drops of HCl added. Benzyl iodide (3.72 g.) then added and the mixture refluxed for three and a half hours. On cooling nothing separated out, so a little alcohol was evaporated and orange-yellow oily substance thus obtained was separated. Kept it in the refrigerator overnight but no signs of solidification. As before, it was also taken up in the minimum amount of alcohol and ether (1:1) and shaken with Na_2CO_3 solution. The lower brownish yellow (aq.) layer was separated and acidified with HCl when a brownish yellow precipitate was obtained. This was identified as Diphenacyl-dicarboxylic acid.

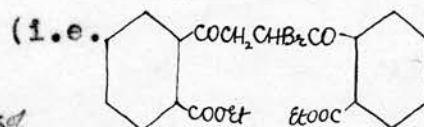
Diphenacyl dicarboxylic acid-diethyl ester and

Bromine:

The /

The ester (0.53 g.) dissolved in glacial acetic acid (10 cc.) was treated with bromine (0.07 cc.). The mixture was warmed, and after the evolution of HBr ceased, the straw yellow solution was cooled, and crushed ice (5 g.) added. The white precipitate was filtered off and attempts were then made to crystallize it by aq. alcohol. A colourless substance, (though not very pure) was obtained (m.p. 94/97°C).

Analysis Found---Calculated for $C_{22}H_{21}O_6Br$



Bromine 18.8% 17.35%

Heating with quinoline (at 170/175°C and 135/140°C) and pyridine (at 115/120°C) gave a yellow orange resinous product which failed to crystallize.

Preparation of Nitrosomethylurea (Arndt and co-workers, Ber.1940,73,607):

Methylamine hydrochloride (50 g.) and Urea (150 g.) dissolved in water (200 cc.) were heated (65/70°C) over a water bath for two hours, and thereafter boiled vigorously for 15 to 20 minutes. Sodium nitrite (55 g.) added and the mixture cooled to -10°C. Concentrated sulphuric acid (55 g.) and ice (300 g.) were added with continuous stirring to the reaction mixture now contained in a 1500 cc. capacity beaker and surrounded by an ice-salt mixture. Addition was made at such a rate that the temperature never went /

went above 0°C. Nitrosomethylurea separated as a foamy crystalline precipitate which was filtered off at once over suction and sucked as dry as possible. Dried in a vacuum desiccator over CaCl_2 and kept in the refrigerator.

For a quick preparation of Diazomethane:

(Arndt, Org. Syntheses, Vol.15, 3, (1935))

the following procedure was employed.-

A mixture of 40% KOH (30 cc.) and ether (100 cc.) was cooled to 5°C and to it with continued shaking and cooling was added powdered nitrosomethylurea (10 g.) in small proportions over a period of two to three minutes. The deep yellow ethereal layer was separated and dried over KOH pellets.

Diphenacyldicarboxylic acid and diazomethane:

Diphenacyldicarboxylic acid (7 g.) dissolved in acetone (20 cc.) was treated with an ethereal solution of diazomethane (2 g. of the latter in 70 cc. of ether), the latter being added over a period of five to seven minutes. After fifteen minutes the reaction mixture was warmed whereby any excess of diazomethane was removed along with ether. The solution was evaporated to dryness when an almost colourless substance, (a faint pinkish tinge) was obtained. Crystallization from methanol gave colourless needles, (m.p. 79/80°C). Yield = 7.23 g. of pure material.

Analysis /

Analysis:	Found	Theoretical (for $C_{20}H_{18}O_6$)
Carbon	68.23%	67.98%
Hydrogen	5.09%	5.1%

Reaction with bromine: The dimethyl ester (2.0 g.) dissolved in glacial acetic acid (15 cc.) was treated with bromine (0.30 cc. - 1 mol.) and the solution warmed to about 50-55°C. HBr was liberated and the solution turned pale yellow. Cooled and treated with ice (15 g.) when a pale yellow resinous product was obtained. It was separated and triturated with 10-15 cc. of methylalcohol when a colourless crystalline substance was obtained. Recrystallization from methylalcohol gave colourless crystals m.p. 107/108°C.

Analysis	Found	Theoretical (for $C_{20}H_{17}O_6Br$)
Bromine	18.7%	18.47%

Removal of HBr.:

(1) By heating with quinoline at 150-160°C:

0.1 g. of the bromo-intermediate with 2 cc. of quinoline heated at 150-160°C for half an hour. Cooled and poured into 25 cc. of dilute HCl when a dark brown resinous product was obtained. This could not be crystallized.

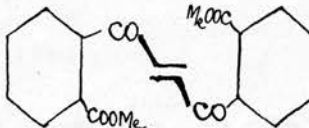
(11) By heating with quinoline at 120/130°C did not improve the matter much. Again a deep brown resinous product was obtained and which could not be purified.

(111) /

(111) By heating with Pyridine at 120°C :

0.20 g. of the bromo-compound and dry pyridine (3 cc.) were heated for twenty minutes at 120°C . The original pale yellow turbid solution changed to a deep orange (clear) solution towards the end of the reaction. Cooled and poured into 35 cc. of dilute HCl and the orange-yellow precipitate filtered off, washed well with water and crystallized from methylalcohol, when pale yellow needles were obtained (m.p. = $109/110^{\circ}\text{C}$ and m.m.p. with the bromo-intermediate = $93/94^{\circ}\text{C}$).

It is fairly soluble in most of the solvents but sparingly so in light petroleum. Analysis Found Theoretical (for $\text{C}_{20}\text{H}_{16}\text{O}_6$)

			i.e.	
Carbon	68.08%	68.18%		
Hydrogen	4.56%	4.54%		

Yield = 0.158g of pure substance (corresponding to 97% of theoretical).

Hydrolysis of the ester: 1. By 10% NaOH solution:

The dimethyl ester thus obtained, (0.158g) was treated with a cold solution of 10% NaOH (aq. solution 10 cc.). The mixture was slightly warmed and the clear orange brown solution after cooling was acidified with dilute HCl. A yellowish orange precipitate was obtained. Filtered, but it soon turned to /

to a brownish orange sticky mass, which could not be purified.

(11) (more ester was prepared for further investigations).

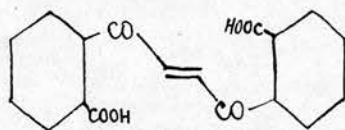
Hydrolysis with 5% NaOH solution: This dimethyl ester (0.1 g.) was next treated with 5% aq. NaOH solution and the mixture left at room temperature for two hours. Some of the ester had gone into solution, and after a very gentle warming (about 40°C) for twenty minutes, the solution became clear orange brown. It was cooled and acidified with dilute HCl. As before, a yellowish orange precipitate was obtained which could not be crystallized out.

(111) Hydrolysis with dilute HCl:

The ester (0.35 g.) was refluxed with dilute HCl (15 cc. of concentrated HCl diluted with 25 cc. of water) for three hours. Cooled and the yellowish orange solid filtered off. Crystallization from glacial acetic acid gave a yellow substance (m.p. 312/313°C corr.).

Analysis gave: C = 70.68% and H = 3.56%

whereas for $C_{18}H_{12}O_6$



the values are:

C = 66.7% and H = 3.7%

*C₁₈H₁₀O₅
C, 70.6; H, 3.7%*

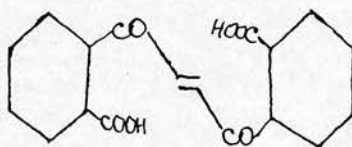
Hydrolysis by boiling the ester (0.1 g.) for one hour with dilute HCl (10 cc. and alcohol (10 cc.) also gave no useful result. A yellowish orange substance was obtained which was difficult to be purified from the ordinary solvents.

Hydrolysis with 1% aq. NaOH solution:

The ester (0.33 g.) was treated with 1% aq. NaOH solution (60 cc.) and the mixture gently warmed till the whole of the ester went into solution. The solution was filtered, and after cooling it was acidified with HCl when an orange red precipitate was obtained. It was filtered under suction and kept over CaCl_2 in vacuum, since in a wet state it had a tendency to turn deep red in colour. Melting point of the crude substance = $152/155^\circ\text{C}$. uncorr. Analysis was not carried out since no satisfactory crystallization was possible.

The formation of the acid was, however, established by treating the orange red product obtained above with thionyl chloride. There was effervescence and after the visible reaction had ceased, all the unreacted thionyl chloride was driven off when the acid-chloride was left behind as a deep red substance (soluble in benzene). A sodium fusion test of this substance clearly showed the presence of chlorine.

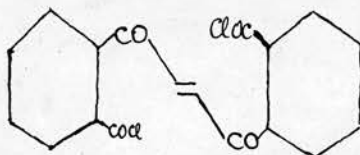
The acid



(0.1 g.) was next dissolved in conc. H_2SO_4 (20 cc.) and the mixture covered with a layer of chloroform (25 cc.). After warming the mixture to about $35/40^\circ\text{C}$, sodium /

sodium azide (about 0.05 g.) was added and the mixture shaken well. After leaving overnight at room temperature, the mixture was decomposed by pouring it on to crushed ice and after filtration a very dark brown sticky substance was obtained. Evaporation of chloroform also yielded a very small amount of a similar product but purification of both the products was difficult.

In another experiment, when the "acid chloride"



dissolved in benzene, was gently heated with dry powdered sodium azide, and the reaction mixture subsequently decomposed by HCl a brownish tarry product was obtained after the evaporation of benzene which also could not be purified.

Preparation of 3-3' Dinitro-ethinedipthalide:

After several experimental trials, the following procedure was found to give the best results. In other cases, employing different periods of time for heating, which varied from two to four hours, some 3-nitro-phthalic anhydride was recovered when the temperature was kept below 200°C, while above 235-240°C the whole yielded very dark coloured products whose purification was rather tedious.

3-Nitro phthalic anhydride (10 g.) and succinic acid (8 g.) were fused together at a temperature of 195 - 200°C) and 4 g. of dry powdered potassium acetate gradually added with a slight swirling around of the reaction mixture. The temperature was then raised to 215/222°C and after about fifteen minutes an orange brown crystalline substance began to separate from the original orange brown clear melt; the mixture being maintained at this temperature for two hours. The mixture was cooled, treated with 50 cc. of warm water, filtered and the dark brown residue crystallized from nitrobenzene when 0.8 g. of a yellow crystalline substance (m.p. above 350° micro apparatus) was obtained.

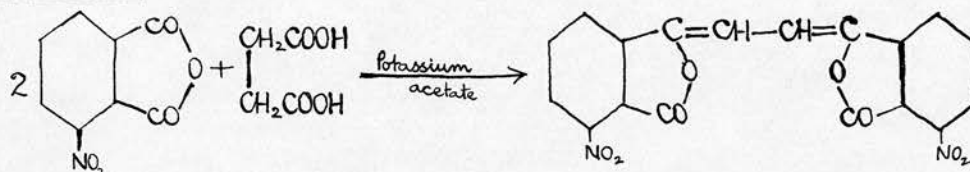
Yield - about 8%

Analysis Found Theoretical for $C_{18}H_8O_8N_2$

Carbon	57.98%	57%
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Hydrogen	2.15%	2.1%
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Although the found value of carbon is higher than the theoretical, the reaction can be represented as follows:-



Since the yields were poor, the experiment was next repeated with 4-nitrophthalic anhydride.

Preparation of 4-4' Dinitroethinedipthalide:

4-Nitrophthalic anhydride was obtained by heating 4-nitrophthalic acid (25 g.) at 165-170°C for four hours. (Walter Lawrence, J.A.C.S. 1920, 42, 1871). After cooling the pale brownish reaction product was dissolved in hot acetyl chloride, evaporated to dryness and recrystallized from glacial acetic acid, when 16 g. of pale yellow crystals were obtained (m.p. 114/115°C).

Yield = about 70%

4-Nitrophthalic anhydride (10 g.) succinic acid (8 g.) were heated together at 180°C and 4 g. of dry potassium acetate added to the pale brown fused mass. The temperature was then raised to 205/210°C and the mixture maintained at this temperature for two and a half hours when a dark brown substance separated out. Cooled and treated, the reaction mixture with 50 cc. of warm water, filtered and the dark brown residue crystallized from nitrobenzene when a yellow crystalline substance was obtained (m.p. above 350°C on micro apparatus).

Yield /

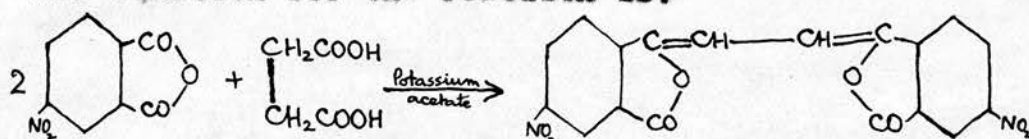
Yield = 5.3 g. equivalent to about 53%

Analysis Found Theoretical for $C_{18}H_{18}O_4N_2$

Carbon 57.5% 57%

Hydrogen 2.3% 2.1%

The equation for the reaction is:



4-4' Dinitroethinediphtalid obtained as above was gently warmed over a water-bath with aq.KOH solution (10%). After half an hour the clear yellowish-brown solution was cooled, filtered and acidified with HCl when a brownish-yellow gelatinous precipitate was obtained. Further investigations had to be abandoned since the acid itself could not be purified from ordinary organic solvents nor did the esterification by using diazomethane give any help.

- DISCUSSION -

PREPARATION OF FUMARYLCHLORIDE: Hans Meyer

(Monatsh, 1901, 22, 415) in a series of experiments obtained various acid chlorides by the use of thionylchloride. He also reported that fumaryl chloride could be obtained by a similar procedure but W.A. and G.C.A. Van Dorp (Rec., trav. chim., 1906, 25, 96) stated that Meyer's method was quite unsatisfactory. Further contradiction of Meyer's work, in so far as the preparation of this acid chloride was concerned, came from McMaster and Ahmann (J.A.C.S. 1928, 50, 145) who said that with thionylchloride, maleic acid gives the anhydride whereas fumaric acid is recovered unchanged.

During the course of this research, where frequent preparations of fumarylchloride were necessary, a careful re-examination of the mode of preparation of this reagent was deemed advisable. After several experiments it was established that thionylchloride does not react with fumaric acid and as is already known, maleic acid yielded its anhydride when heated with thionylchloride. Variations in the procedure were equally unsuccessful. When the work was practically complete, it was found that Coulson too, (J.C.S. 1934, 1410), had obtained similar results, in that he also found that thionylchloride does not react with fumaric acid. It should also be admitted, however, /

however, that Van Dorp's method (*loc.cit.*) is tedious and cannot be recommended for frequent preparations of the acid chloride.

Kyrides (J.A.C.S.1937,59,206) obtained fumarylchloride from maleic anhydride and phthalylchloride in the presence of a little zinc chloride. Attempts to obtain fumarylchloride from fumaric acid and thionylchloride in presence of a little zincchloride were unsuccessful.

Fumarylchloride was also obtained by Perkin (Ber.14,2548) from maleic anhydride and PCl_5 . The method however is unsatisfactory since much of the anhydride is left unreacted at end of the reaction. The only satisfactory method for obtaining the acid chloride conveniently, is from fumaric acid and PCl_5 (Kekulé, Ann.Suppl.1862,2,86, Von Auwers, Ber.1913,46, 480). Fumaric acid with a slight excess of the theoretical amount of PCl_5 , is heated over a water bath for thirty to forty minutes and the clear solution after quick decantation is fractionally distilled. Phosphorous oxychloride distills over first, but a redistillation of the later fraction gives sufficiently pure fumarylchloride.

PREPARATION OF DIBENZOYLETHYLENE AND SUBSTITUTED DERIVATIVES: For this purpose several procedures have been tried. The Friedel-Crafts synthesis with fumarylchloride (Conant and Lutz, J.A.C.S.1923,45,1303) is one of the most convenient to manipulate. Since most of the other methods involve either just as inaccessible /

inaccessible starting materials and the process is tedious.

Apart from throwing fresh light on previous investigators' work, two of the schemes proposed for the preparation of dibenzoylethylene and their substituted derivatives, dealt with in this thesis, are other methods of approach to the preparation of all such compounds.

Following the failure of Weygand and Lenzendorf (J.pr.Chem.1938,151,205) to repeat Smedley's work (J.C.S.1909,95,219) and thus obtain dibenzoylethylene (from Phenylglyoxal and acetophenone by heating with an excess of acetic anhydride), the experiment was repeated in attempts to obtain di-(p-methoxybenzoyl) and di(p-bromobenzoyl)ethylenes.

In the first case, p-methoxyacetophenone and p-methoxybenzoylformaldehyde were heated together with an excess of acetic anhydride. A colourless substance was obtained which was not di(p-methoxybenzoyl)ethylene. Heating p-methoxyacetophenone and p-methoxybenzoylformaldehyde with glacial acetic acid containing a trace of conc. H_2SO_4 yielded a brownish orange resinous product which could not be crystallized.

In the second experiment, however, the yellow ^{of} isomer/ di(p-bromobenzoyl)ethylene was obtained when p-bromoacetophenone and p-bromobenzoylformaldehyde were /

were refluxed together in glacial acetic acid containing a trace of H_2SO_4 , but attempts to obtain $BrC_6H_4COCH(OOCCH_3)CH_2COOC_6H_4Br$ by using acetic anhydride (Smedley loc.cit.) were unsuccessful.

This result is in keeping with the views already advanced by Weygand and Lanzendorf that glacial acetic acid containing a trace of conc. H_2SO_4 should be used and not acetic anhydride as suggested by Miss Smedley.

Selenium dioxide oxidation of saturated 1,4-diketones:

By analogy with the selenious acid oxidation of acetonylacetone (Armstrong and Robinson, J.C.S. 1934, 1650) and ethylsuccinate (Astin, Riley and Newman, J.C.S., 1933, 391), the possibility suggested itself of obtaining the various unsaturated 1,4-diketones, by oxidation of the corresponding saturated diketones with SeO_2 . Working in this direction, it has been possible to obtain the yellow isomers of dibenzoyl, di-p-tolnyl, di-p-chlorobenzoyl and di-p-bromobenzoyl-ethylenes by refluxing the corresponding saturated compounds with a little excess of SeO_2 in 95% alcohol.

A noteworthy feature of this series of experiments was, that when a little HCl was added to the reaction mixture, the time required was less and in some cases the yields were also increased. Although in the main, attention was confined to see whether the saturated γ -diketones could be oxidised by this reagent (SeO_2) to yield the corresponding unsaturated derivatives, there is reason to believe that increased /

increased yields can be obtained by a longer period of heating, particularly if hydrochloric acid is present. The role of HCl thus becomes significant. That it helps to increase the yields may be explained by the fact that under its influence any colourless isomer which might have been produced undergoes rearrangement into the trans-form, while its function in accelerating the oxidation is supported by the recently published work of Melnikov and Rokitskaja (J.Gen.Chem.Russ., 1944, 1054-1058; Br.C.A. November 1946, p.352) that the velocity ^{of oxidation} of COMe_2 by $4\text{N-H}_2\text{SeO}_3$ is proportional to the hydrogen ion concentration of the solution. 4-4'-Dimethoxydiphenacyl, however, was abnormal in its behaviour towards SeO_2 oxidation. An orange oil, (unsaturated and not enolic in character) was obtained, which could not be purified, and with thionyl chloride gave a deep red colouration.

PREPARATION OF UNSATURATED 1,4-DIKETONES BY THE
REMOVAL OF HBr from α -brom- α - β -DIAROYLETHANES:

It is an established fact that of the three halogen-diphenacyls (α -, β - and γ -) that are known, it is only the γ -variety in which HX can be easily removed (X = halogen), and Paal and Schulze (Ber., 35, 172) showed that removal of hydrogen-halide from such compounds may be done by using an alkali-acetate when the yellow isomer of dibenzoyl-ethylene is obtained.

Of the several agents employed for the removal
of /

of hydrogenhalide, usually all are of a basic nature. Generally KOH or NaOH is sufficient while sometimes the alcoholates or alkali acetates (as pointed out above) are more useful. Organic (basic) solvents have also occasionally been used. In the present work, the use of pyridine and quinoline among such reagents has been investigated to demonstrate their applicability for the preparation of unsaturated 1,4-diketones from α -bromo- α - β -diaroyl ethanes. The latter are easily obtainable from the saturated 1,4-diketones and bromine (an account follows in the succeeding pages).

The method can be regarded as a standard procedure, the yields are almost quantitative and the resulting products are obtained in a good state of purity. The procedure may be conveniently employed to prepare even a few milligrams of the desired product.

The most satisfactory procedure is to heat α -brom, - α - β -diaroyl ethane with twice its weight of quinoline at 170/180°C (usually in an oil bath). One or two preliminary experiments are sufficient to estimate the temperature at which the reaction mixture should be heated. Sometimes it is necessary to heat the reaction mixture at lower temperatures (about 130°C or so) and in such cases the use of pyridine instead of quinoline is recommended. Usually twenty minutes suffice for the reaction to go to completion, and the resulting orange-yellow viscous solution, after being cooled to about 50°C is poured into dilute /

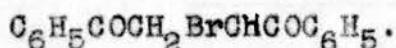
dilute HCl (a hydrochloride of the base, i.e. pyridine or quinoline is thus produced) and after about half an hour the yellow precipitate is filtered off and crystallized from suitable solvents.

PREPARATION OF γ -BROMDIPHENACYL:

α -brom, - α - β -diaroylethanes have hitherto been prepared by the addition of HBr to trans-diaroylethylenes in warm glacial acetic acid. It appeared to us to be of considerable interest to prepare these brom compounds by reacting diphenacyl or substituted derivatives (1 mol.) with bromine (1 mol.) in warm glacial acetic acid, and α -brom - α - β -dibenzoylethane thus prepared has been found to be identical, by its analysis and mixed m.p., with a genuine sample of α -brom, α - β -dibenzoylethane.

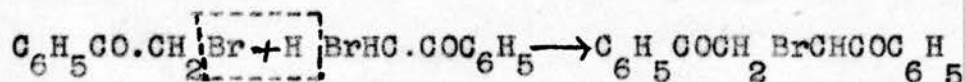
Likewise when two molecules of bromine were employed for one molecule of diphenacyl, α - β -dibrom, α - β -dibenzoylethane, m.p. 177°C was produced. The other isomeric dibromide which might have been produced in very minute quantity could not be isolated, however, (cf. Lutz, J.A.C.S. 1926, 48, 2905)

These are simple cases of bromine substitution for hydrogen of the $-\text{CH}_2$ groups in the diphenacyl molecules; and the configuration of compounds of this type (i.e. α -brom- α - β -dibenzoylethane) is clear in that they are to be regarded as true dibenzoylethane derivatives, and represented as /



The ready removal of hydrobromic acid from γ -bromdiphenacyl^{is shown by its} reaction with alkali acetates etc. to give the yellow isomer of dibenzoylethylene whereas the reaction between γ -bromdiphenacyl and hydrazine hydrate yields 3:6 diphenylpyridazine as in the case of 1:4-diketones.

For the other two halogendiphenacyls, obtained by the action of NaOEt on phenacyl bromide, a different picture presents itself. Paal and Schulze (Ber., 35, 168, 36, 2411) had described these to be the geometrical stereoisomers of the formula $\text{C}_6\text{H}_5\text{C}(\text{OH})\text{:C}(\text{X})\text{.CH:C}(\text{OH})\text{C}_6\text{H}_5 \rightarrow (\text{X stands for halogen})$. Fritz. (Ber., 1895, 28, 3028) assumed that a carbon-carbon linkage was brought about with the simple elimination of HBr.

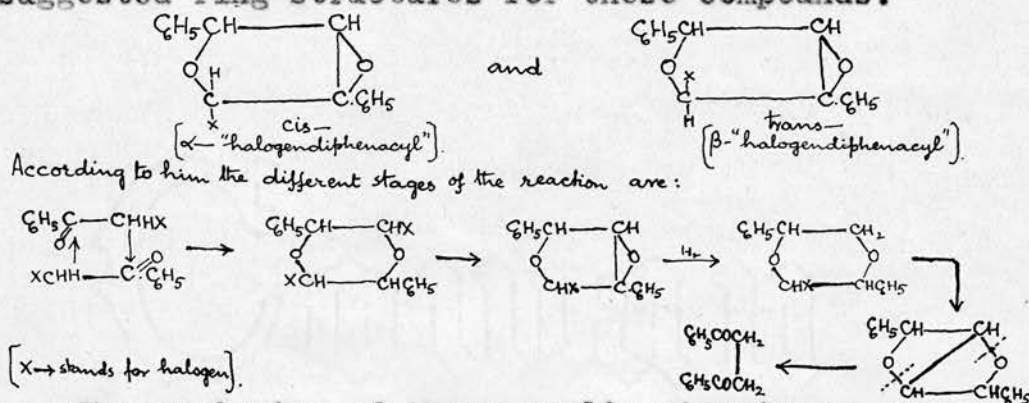


Assumptions like these, brought forth criticism from Oskar Widman, who, (Ber., 1909, 42, 3261; Annalen, 1913, 400, 86) argued that if Fritz's assumption was correct, then, under the action of an excess of NaOEt, both the halogens should have been eliminated and dibenzoylethylene formed which, of course, is the case with γ -bromdiphenacyl. As pointed out by Widman (loc.cit.) Fritz was wrong, since $\text{C}_6\text{H}_5\text{COCH}_2\text{BrHCCOC}_6\text{H}_5$ represents γ -bromdiphenacyl which is a true diketo-derivative since it reacts with $\text{NH}_2\text{.NH}_2$ to form 3:6 diphenylpyridazine while /

while α - and β -halogendiphenaclys do not react with the usual ketonic reagents.

With regard to Paal and Schulze's suggestion, the same author, (Widman, loc.cit.) drew further attention to properties of these (α -and β -)halogen diphenaclys such as their inability to decolourize bromine or KMnO_4 or react with acetic anhydride or ferric chloride etc. Only positive would have justified the presence of double bonds and $-\text{OH}$ groups as assumed by Paal and Schulze.

In attempts to explain these anomalies, Widman suggested ring structures for these compounds.



The assigning of these cyclic structures, as Widman pointed out, could explain most of the anomalies in the behaviour of these α - and β -halogendiphenaclys.

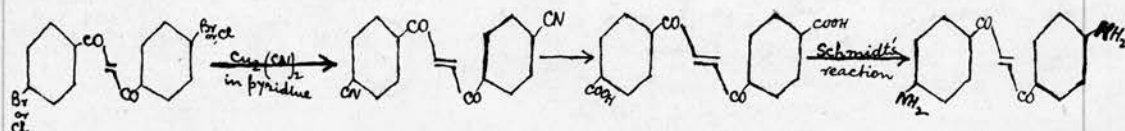
Widman's theory is ingenious in so far as it concerns the halogendiphenaclys, but the assumption that a stable para-linkage is produced during the course of reduction of halogendiphenaclys to diphenacyl seems to be hardly credible as in such a case the carbon to carbon distance will be about 2.8\AA , which is not possible since the known value of the carbon-carbon single bond is 1.54\AA .

Before proceeding further mention may also be made /

made about Ajello's work. This investigator, (Gazz.Chim.Ital., 1937, 67, 608., C.A. 1938, 32, 4566) claimed to have obtained $C_6H_5COCH_2BrHC.CO.C_6H_5$ (i.e. γ -bromdiphenacyl) from $C_6H_5COCH_2Br$ by using aq. KOH instead of NaOEt. It is also an established fact that when NaOEt is used β -bromdiphenacyl is the resulting product. No doubt, the various halogen-diphenacyls can be converted into diphenacyl by reducing with magnesium powder (γ -variety being reduced more easily than the β -variety), yet Ajello's work appeared to us to be faulty and a repetition of his work has revealed that a mixture of α - and β -bromdiphenacyl is produced, which we were able to separate easily by using benzene.

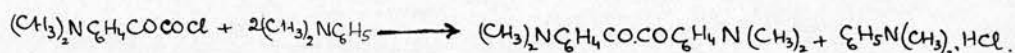
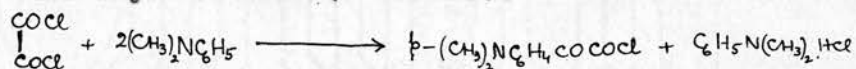
As stated before, it was proposed during the course of this research to prepare some unsaturated 1,4-diketones with certain auxochromic groups present. Several "syntheses" have been attempted and though it is unfortunate that compounds like di(o,m, or p-aminobenzoyl)ethylenes could not be prepared, some interesting information has been obtained about the general behaviour of the compounds of this class.

The first synthesis of the several tried, was planned as follows:



The very first stage of the process unfortunately was found to be unsatisfactory, since no di(p-cyanobenzoyl)ethylene could be isolated. The method was therefore abandoned.

The next idea was to react dimethylaniline with fumaryl chloride. In a comparable reaction, Standinger and Stockmann (Ber., 1909, 42, 3485) obtained tetramethyldiamino-benzil from oxalyl chloride (1 mol.) and dimethylaniline (4 mols.):



Working along the same lines, the reaction between fumarylchloride (1 mol.) and dimethylaniline (4 mols.) using benzene as the diluent met with no success; an almost black substance being obtained which could not be purified by ordinary organic solvents.

In another series of experiments, condensations of the various nitroacetophenones with phenylglyoxal in glacial acetic acid containing a trace of H_2SO_4 were attempted in the hope of obtaining the corresponding mono-nitro-dibenzoylthylenes and from which it was planned to prepare the corresponding mono-amino-dibenzoylthylenes by reducing with reagents such as $(\text{NH}_4)_2\text{S}$ etc. In the case of the meta-derivative much of the m-nitroacetophenone was recovered along with resinous products while for the para-compound a yellow substance (call it A), m.p. 145/146° C was obtained together with some p-nitroacetophenone. Treatment of A with hydrazine hydrate gave a substance melting at 234° C but its analysis, as well as that of A did not indicate them to be the desired products.

Condensations of p-N-acetylaminoacetophenone with phenylglyoxal and m-nitroacetophenone with m-nitro-benzoylformaldehyde were also unsuccessful.

Because of the ease of obtaining trans-isomers of diaroylethylenes from the corresponding diaroylethanes, attempts were next made to obtain mono- and dinitrodibenzoylethanes.

Perkin and co-workers (J.C.S. 1886, 49, 453; 1904, 85, 148) prepared diethyl di-ortho and para-nitrobenzoylsuccinates. It appeared to us that hydrolysis of such compounds might give the corresponding diphenacyls since Knorr and Scheidt (Ber., 1894, 27, 1168) obtained diphenacyl by hydrolysing ethyldibenzoylsuccinate. Hydrolysis of diethyldimeta and diparanitrobenzoyl succinates, however, yielded only the corresponding nitrobenzoic acids ("Acid hydrolysis" having taken place).

3% yield at
water-bath temp.
occurs readily,
but no yield
given.

The method of Bodforss was then applied to obtain different mononitrodibenzoylethylenes. In a preliminary experiment his work was repeated and diphenacyl in very good yields was obtained. The reactions between benzoylacetone and ω -monobromo-(o,m, and p-nitro)-acetophenones presented difficulties, as anticipated, due to the presence of the nitro group. An instantaneous precipitation took place in each case, and all attempts to purify these compounds were unsuccessful as were the attempts to obtain anything substantial by hydrolysis of these impure products (and thus isolate the corresponding mononitrodibenzoylethanes).

In a similar series of reactions, the initial preparation of p-nitrobenzoylacetate from methyl/

methy1-p-nitrobenzoate and ethyl acetate in presence of NaOMe did not succeed. This nullified the plan to react the sodium compound of the resulting ester with phenacylbromide in order to obtain phenacyl, (o-m- or p-nitrobenzoyl)acetic ester and from it the saturated diketones, although the possibility of acid hydrolysis could also be anticipated, since Kapf and Paal (Ber. 21, 1487, 3056) obtained benzoic and benzoylpropionic acids by heating phenacylbenzoylacetic ester with aq. KOH. It is however hoped, to prepare p-nitrobenzoylacetic ester by Claisen's method as extended by Perkin and co-workers (loc.cit.)

Grignard reaction between Phenylmagnesiumbromide and fumaric and succinonitriles:

The reaction between a nitrile and Grignard compound (R.Mg.X) is known to result in the formation of a ketone. On this basis, reactions between PhMgBr and fumaric, succinonitriles were tried in attempts to obtain the corresponding diketones for which there exists no record in the literature.

In the actual experiments, however, no diketones could be isolated, even when several modifications were employed. Shriner and Turner (J.A.C.S. 52, 1268) recommend the use of four molecules of the Grignard compound per every molecule of the nitrile, although the significance of this procedure is unknown. (In our case, eight mols. of Ph.Mg.Br. were thus necessary). As said above, all variations in the procedure (like decomposing with ice cold NH_4Cl and HCl, using eight mols. of Ph.Mg.Br. etc.) yielded no satisfactory results, /

results, and dark resinous products were invariably obtained which is perhaps due to these nitriles polymerizing under the action of the Grignard compound. In the reaction between succinonitrile and Ph.Mg.Br. a minute amount of diphenyl was obtained.

Bogoslovskii's method for the preparation of sym-dibenzoylethylene, (J.Gen.Chem.U.S.S.R., 14, 993-4; C.A.39, 4600(1945) is another procedure which can be employed conveniently for the preparation of this compound. The reaction involves the treatment of phenacyl chloride dissolved in warm alcohol with aq. KOH, and subsequent treatment with water.

During several preliminary experiments (and also found later on - J.C.A.(British), 1946, 597) it was observed that the success of the method was dependent upon the quick working of the reaction products after the mixture had been added to water, otherwise resinous products are obtained whose purification becomes extremely tedious.

The application of this method, in attempts to prepare di-(meta and para-nitrobenzoyl)ethylenes gave unsatisfactory results; but in the case of the ortho-compound, a colourless product was obtained, though in small yields, and which by analogy to the known cases, was thought to be the cis-isomer. Its analysis corresponded to that of the desired product, namely, cis-di(o-nitrobenzoyl)ethylene but due to its unsatisfactory results with hydrazinehydrate, further investigation of this compound was abandoned. It is, however /

however, proposed to examine this compound closely, since the other methods of preparing di(o-nitrobenzoyl)ethylenes have failed. A preliminary experiment, on a few milligrams scale has indicated that it adds on HBr and from the intermediate bromo compound, heating with quinoline at 150°C gives an orange resinous product. It is hoped that by employing pyridine instead of quinoline and maintaining the temperature about 100 or 120°C, may yield useful results.

During the course of other experiments, in order to prepare sym-di(p-methoxybenzoyl)ethylene from ω-chloro-p-methoxyacetophenone and aq.KOH by an identical procedure as outlined before, a colourless substance was obtained whose analysis revealed that it was presumably an epoxide (i.e. $\text{H}_3\text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH} \cdot \text{CH} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OCH}_3$) ~~$\text{CH} \cdot \text{CH} \cdot \text{COO} \cdot \text{C}_6\text{H}_4 \cdot \text{OCH}_3$~~ . Lutz and Wilder (J.C.S. 1934, 56, 1987) had prepared an identical compound, namely dibenzoyl ethylene oxide by the action of H_2O_2 on both cis- and trans dibenzoyl ethylenes, and it may be of interest to extend their method further so as to obtain the various other epoxides.

With the failure of all these methods, attention was then directed towards another method in the hope of preparing di(o-aminobenzoyl)ethylene.

Gabriel and Michael (Ber., 1877, 10, 1559) obtained diphenacyldicarboxylic acid by treating ethine-diphthalide with an alkali. Ethinediphthalide itself is readily prepared by condensing phthalic anhydride with succinic acid in presence of an alkali-acetate (Gabriel /

(Gabriel and co-workers, Ber., 1877, 10, 1559; 31, 1160). Diphenacyldicarboxylic acid, as is evident, is to be regarded as a derivative of the saturated -diketone class and by the quinoline (or pyridine) dehydrohalogenation method already worked out, it was hoped to obtain the corresponding unsaturated compound. The acid was for this purpose first esterified.

Esterification: The usual methods for accomplishing esterification of the acids include either heating the acid with alcohol and a little H_2SO_4 or passing dry HCl gas into an alcoholic solution of the acid. When these procedures were adopted, practically no success was achieved. By passing dry HCl gas for four hours into an ethyl alcoholic solution of diphenacyldicarboxylic acid, ethinedipthalide was obtained, (indicated by analysis, and m.p. which was above $350^{\circ}C$). Rose^r (Ber., 18, 3116) had obtained similar results also. In the other procedure, when the acid was refluxed in ethanol solution with a little H_2SO_4 , (concentration of the latter being about 8-10%) a very small amount of a colourless substance was obtained whose analysis indicated it to be the expected diethyl ester, but most of the acid was recovered unchanged. Treatment of this diethyl ester with bromine did not give very promising results. There was yet another possibility, namely, that it might be the anhydride of diphenacyldicarboxylic acid Roser (Ber., 18, 3116) quotes the melting point of the anhydride as $200-202^{\circ}C$ which is very much the same as that /

that of our product. The analysis of the bromo-intermediate compound prepared by us though not in a pure state, however, favours the conclusion that a diethyl ester had been produced since the value for Br_2 , assuming the anhydride to have been formed, is still ~~farther~~ different from the theoretical value (for which it is = 20.6%), while the tendency of the acid to undergo lactonization during the "HCl" method, indicates the possibility of the anhydride formation. When diphenacyldicarboxylic acid was heated with alcohol and a little H_2SO_4 for a longer time, then along with the colourless substance (m.p. 202°C) a small amount of ethinedipthalide was also produced. It was then decided to employ diazomethane to accomplish the esterification.

Diazomethane itself was obtained from nitrosomethylurea and aq. KOH solution. For esterifying the acid, it was dissolved in acetone and treated with a dry ether-solution of diazomethane. A slight excess of the latter was employed and the dimethyl ester was obtained in a high state of purity as colourless needles. The yield was quantitative.

Preparation of Di-o-carbomethoxy-dibenzoylethylene:

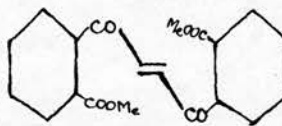
The dimethyl ester of diphenacyl dicarboxylic acid, obtained as above, (1 mol.) was as usual treated with one mol. of bromine in warm glacial acetic acid. As expected, HBr was liberated and the bromo compound obtained from the solution, was proved to be the desired product by its analysis.

The next stage was the removal of HBr. For this

purpose/

purpose, after some preliminary experiments, it was found that heating with pyridine at 120/130°C. gave the best results. At higher temperatures and heating with quinoline gave resinous products.

Hydrolysis of this compound



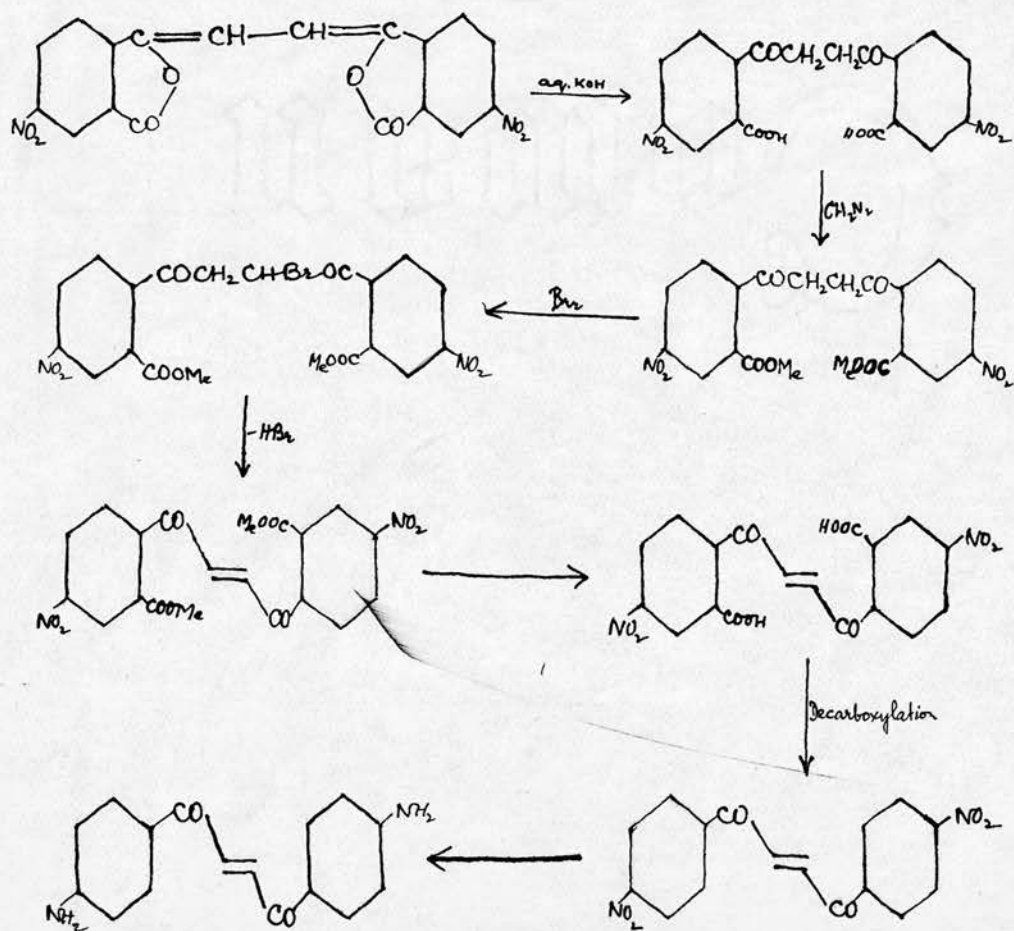
gave poor results. With HCl, no useful purpose was served. The ester went into solution upon gentle warming with aq.KOH, and subsequent acidification with HCl an orange-red precipitate which could not be easily purified. The substance, probably free acid, in a wet state, on continued exposure to air had a tendency to develop an intensely red colour, but appeared to be quite stable after it had been put over CaCl_2 in vacuum overnight. Being impure it could not be analysed.

Further confirmation about the formation of the acid was obtained by preparing its acid chloride using thionyl chloride. There was an effervescence, when SOCl_2 was added and after the reaction was complete, all the SOCl_2 was driven off when a deep red residue was obtained, (fairly soluble in benzene). A sodium fusion test clearly established the presence of chlorine.

Attempts to obtain the amino derivative from the acid chloride through the intermediate formation of the acid azide and by treating a H_2SO_4 solution of the acid itself with sodium azide, (see Sidgwick: Org.Chemistry of Nitrogen -p.370-377) were all fruitless.

Following /

Following the failure of this plan, 3- and 4-nitrophthalic anhydrides were next condensed with succinic acid in the presence of potassium acetate. 3-3'-dinitroethine diphthalide and 4-4'-dinitroethine diphthalide were thus obtained and identified by their analysis. The yield of the former was however very low. Further treatment of 4-4'-dinitroethine diphthalide with aq. KOH and subsequent acidification yielded a small amount of a gelatinous precipitate, but attempts to obtain it pure by esterifying first with diazomethane were unsuccessful. The plan of this synthesis being:



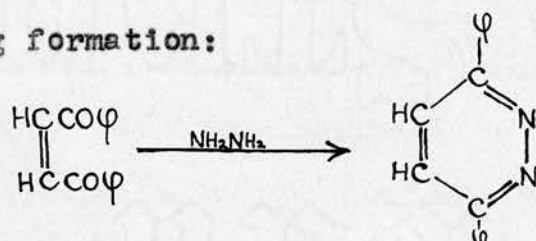
THE CONFIGURATIONS OF THE ISOMERIC DIBENZOYL-ETHYLENES AND THEIR SUBSTITUTED DERIVATIVES:

Paal and Schulze's method of distinguishing between the cis- and trans isomers of dibenzoyl-ethylenes using hydrazine hydrate has been re-examined during the present work and further evidence has been obtained to confirm their results.

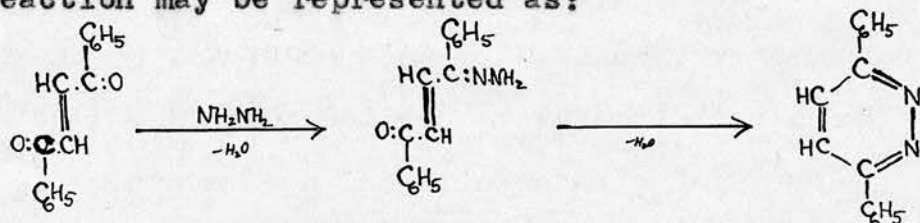
Following Weygand and Lanzendorf, who extended this reaction to the isomeric pairs of several unsaturated 1,4-diketones (J.pr.Chem.1938,151,220), a further comparative investigation of the same reaction during the course of this work with the isomeric di-p-chlorobenzoyl and di-p-bromobenzoyl-ethylenes with glacial acetic acid as the solvent (solubility of the yellow isomers in alcohol being very low at ordinary temperature), revealed that the colourless isomers in each case reacted with hydrazine hydrate to yield a pyridazine derivative while the yellow isomers were recovered unchanged. The latter, however, reacted with hydrazine-hydrate when a mixture of the two was boiled for several minutes.

For the two isomeric dibenzoyl-ethylenes, when alcohol was used instead of glacial acetic acid, treatment with hydrazine hydrate at room temperature followed by leaving the reaction mixture overnight yielded two different products. The colourless isomer, as anticipated, gave 3:6 diphenylpyridazine which was identified by m.p. (which is known) and its analysis. The yellow isomer on the other hand yielded faintly yellow /

yellow plates and analysis of this compound indicated that it was a monohydrazone. It seemed probable that this monohydrazone might be an intermediate compound and which could undergo transformation into 3:6 diphenylpyridazine if more drastic conditions were employed. This was established by heating its solution almost to boiling for a few minutes when 3:6 diphenylpyridazine was obtained which was identified by a mixed m.p. with an authentic sample. This ease of formation of a pyridazine derivative by the colourless isomer can be accounted for, by assigning to the molecule a cis-configuration since this favours the ring formation:



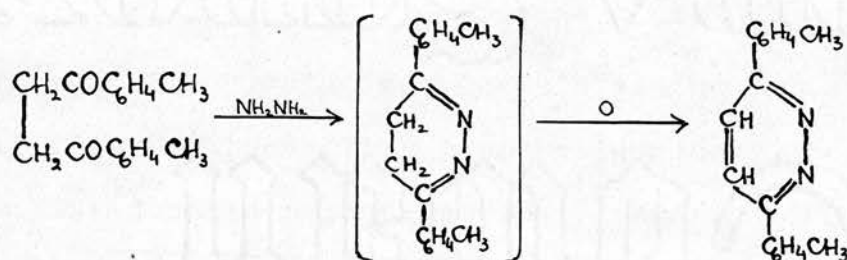
With the isolation of dibenzoyl ethylene monohydrazone, it becomes evident that for the yellow isomer a trans-structure is the more likely and the course of the reaction may be represented as:



It must be admitted, however, that in the case of 3:6 dibromophenylpyridazine, the analysis of the compound was faulty. This is due to the substance being impure, since it has been shown that heating the yellow isomer in glacial acetic acid with hydrazinehydrate for several minutes yielded a product which was identical with the product obtained by treating the colourless isomer /

isomer with hydrazinehydrate (no depression in mixed m.p.), and there appears to be no doubt that 3:6 dibromophenylpyridazine was thus prepared.

The reaction between 4-4'-Dimethyl-Diphenacyl and hydrazinehydrate yielded a product which on being left in contact with air changed into 3:6-di-p-tolnylpyridazine (identified by mixed m.p. with a genuine sample). Obviously this intermediate compound was 3,6 ditolnyl-dihydropyridazine which, being unstable, was oxidized by air into (the stable) 3:6 ditolnylpyridazine:



This result is in harmony with the observation previously recorded by Paal and Dencks (Ber., 36, 495) that diphenacyl and hydrazinehydrate react with each other to form 3,6 diphenyldihydropyridazine and the latter is then oxidized by air to yield 3:6 diphenylpyridazine.

REDUCTION OF UNSATURATED 1,4-DIKETONES:

This section deals with the reduction of dibenzoylethylenes and their substituted derivatives by means of aluminium isopropoxide in isopropyl alcohol, a reagent which is known to attack only the carbonyl groups but which leaves the olefinic linkages intact.

At the outset it was hoped that if the primary dienols formed during the reaction were stable and could be isolated, then it would have been comparatively easier to convert the dienol obtained from the cis-isomer into the corresponding furan derivative than the dienol obtained from the trans-isomer. In fact, in the latter case, the possibility of the formation of a cyclic dimolecular (reduction) product was also considered (cf. Lutz and Palmer etc., J.A.C.S., 57, 1947, 1953, 1957).

The other alternative was, that if the intermediate dienol were unstable then it could either (preferably) rearrange to give a saturated diketone or eliminate water to form a furan.

It has already been shown by Conant, Lutz and co-workers, that the reduction of unsaturated 1,4-diketones in homogeneous solution with soluble reducing agents yields the saturated diketones or the corresponding furans. Under certain conditions the reduction of dibenzoylethylenes with metal combinations or by catalytic hydrogenation also yields diphenacyl or the corresponding substituted derivatives.

The reaction is assumed to involve initially the 1,6-addition of hydrogens to terminal oxygen atoms of the conjugated system, and the primary dienol thus produced then quickly ketonizes to yield the corresponding diphenacyl.

By the reduction of di(trimethylbenzoyl)ethylene at 0°C with zinc and acetic acid and by catalytic hydrogenation at the same temperature in ethanol with platinum as catalyst, Lutz and Revely² (J.A.C.S. 1939, 61, 1854) demonstrated the intermediate formation of the dienol, which though it could not be isolated was moderately stable under those conditions.

It is also known that the addition of reagents other than hydrogen, to unsaturated 1,4-diketones is either 1,2 or 1,4 - but not 1,6. (Gilman's Organic Chemistry, Vol. I (1944), pages 694-699, Allen and Blatt). Thus halogen adds 1,2- to the ethylenic linkage while halogen acids add 1,4- to the system: $C=C-C=O$, the addition products indicating the mechanism to be 1,4- addition with hydrogen entering the molecule at an oxygen atom. The addition of Grignard's reagents to unsaturated 1,4-diketones furnishes 1,4- and occasionally 1,2- addition products.

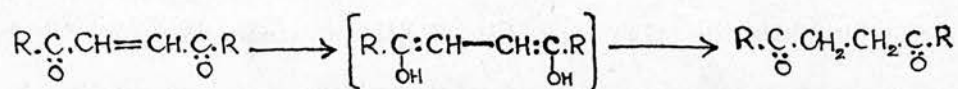
To obtain a correct estimation of the reaction mechanism, both isomers of dibenzoyl-di-p-tolnyl, di-p-chlorobenzoyl, and di-p-bromobenzoyl ethylenes were therefore reduced with aluminium isopropoxide in isopropyl alcohol, and the corresponding saturated γ -diketones were isolated.

Except /

Except *cis*-dibenzoylethylene where the yields are comparatively low, (this matter should be investigated further) an interesting feature was observed that for the *cis*-compound, the yields of the corresponding saturated -diketone (purified by chromatographic adsorption) were 90-95% whereas for the *trans*-compound the yields of the saturated diketone were 70-75%. This incidentally indicates that the *cis*-compound may be regarded as possessing a greater energy content.

Under comparative experimental conditions a minute amount of unreacted yellow isomer was obtained in the reduction of the *trans*-compounds. It is possible that in such cases, since the reaction was slow, towards the end of the reaction the amount of acetone distilling over being very minute, it might not have been detected by 2:4 dinitrophenylhydrazine with the obvious conclusion that the reaction was then thought to be complete.

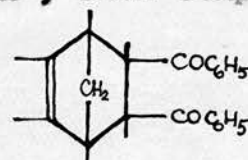
This formation of the saturated diketones is in perfect agreement with the previous findings of Lutz and co-workers. As direct hydrogenation of the carbon-carbon double bond is ruled out, the primary formation of the intermediate dienol is distinctly indicated and the reaction therefore must have proceeded as:



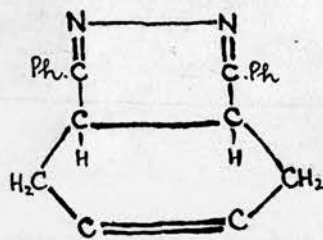
The non-availability of cyclopentadiene has ~~made~~ made it impossible to study the isomeric adducts that /

that could be obtained by the addition of cyclopentadiene to different isomeric pairs of dibenzoylethylenes and their substituted derivatives. Some of these compounds have already been prepared by Roger Adams and co-workers, (J.A.C.S. 1940, 62, 56, 1233)

As outlined in the "introduction", such compounds probably possess the structure



For the adduct obtained by the addition of cyclopentadiene to trans-diaroylethylenes the two aroyl groups are trans- or on opposite side of the ring whereas for the adduct obtained from the cis-isomer, the two aroyl groups can be regarded as lying on the same side. In other words, two aroyl groups are "clamped" in these cases (See also Alder and Stein. (Z. angew. chem. 1937, 50, 510.) for a discussion on similar type of compounds) and by analogy with the reaction between the various isomeric dibenzoylethylenes and hydrazinehydrate, it can be anticipated that the adduct from the cis-isomer, where the two aroyl groups are "clamped", in the cis-position, will react with hydrazinehydrate to yield a pyridazine derivative, (see formula below), while the adduct containing the aroyl groups in the trans-position won't, and as is evident, the configurations of the isomeric dibenzoylethylenes could then be conclusively established.



- S U M M A R Y -

1. Weygand and Lanzendorf's method for the preparation of unsaturated 1,4-diketones has been studied and its advantage demonstrated.
2. Hans Meyer's method of preparing fumarylchloride from fumaric acid and thionylchloride is not correct. Fumarylchloride is best obtained from fumaric acid and phosphorous pentachloride.
3. Attempts to obtain the various amino substituted derivatives of dibenzoyl ethylene by several methods have so far been unsuccessful. If the synthesis of any of these compounds would have been achieved, it would have helped to obtain some insight with regard to the fine structure of indigo.
4. The property that both the methylene groups in saturated 1,4-diketones are equally activated by the proximity of the (negative) carbonyl groups and could be attacked more or less simultaneously has been utilized in the oxidation of diphenacyl and substituted derivatives by selenium-dioxide in alcohol to yield the corresponding trans-unsaturated 1,4-diketones. The effect of HCl as a catalyst has also been demonstrated.

The behaviour of 4-4'-dimethoxydiphenacyl was, however, anomalous, in that no di(p-methoxybenzoyl) ethylene could be obtained.

5. α -Brom- α - β -dibenzoyl and α - β -dibrom- α - β -dibenzoylethanes have been prepared from diphenacyl (1 mol.) and bromine (1 and 2 mols. in respective cases).
6. α -Brom- α - β -diaroylethanes have been successfully dehydrohalogenated by heating with pyridine or quinoline, to yield the corresponding trans-unsaturated 1,4-diketones.
7. The attempted preparation of di(p-methoxybenzoyl)ethylene from ω -chloro-p-methoxyacetophenone and aq.KOH gave a substance which is presumably di-p-methoxybenzoylethylene oxide.
8. The reaction between phenacylbromide and aq.KOH, under the conditions employed by Ajello, has been shown to result in the formation of a mixture of α -and β -bromdiphenacyls.
9. A further comparative study of the reaction between the isomeric dibenzoylethylenes and their substituted derivatives with hydrazine hydrate has confirmed previous investigators' work, that the yellow isomer possesses a trans-structure whereas the colourless isomer has a cis-configuration.
10. By reducing several isomeric pairs of dibenzoylethylene and substituted derivatives with aluminium isopropoxide in isopropyl alcohol, the corresponding saturated diketones have been obtained. The reaction mechanism has thus been definitely shown to /

10 (Contd.)-

to proceed through the 1,6-addition of hydrogen to the terminal oxygen atoms with the intermediate dienol then undergoing rapid ketonization to yield the saturated 1-4-diketone.

- POSTSCRIPT -

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